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THE APPLICATION OF THE CORRESPONDENCE PRINCIPLE TO DEGENERATE SYSTEMS AND THE RELATIVE INTENSITIES OF BAND LINES*

BY EDWIN C. KEMBLE

ABSTRACT

Relative intensities of band lines of a diatomic molecule according to the correspondence principle.—This paper originated in an attempt to harmonize the Kratzer half integral quantum numbers, for which there is strong evidence, with the observed symmetry in the intensities of the two branches of the HCl band at 3.46μ. First the infra-red spectrum of non-gyroscopic diatomic molecules is calculated, *treating the molecule as a degenerate system* with but one quantum condition for two degrees of freedom, following the detailed rules proposed by Kramers. This leads to a formula for the relative intensities of the lines in the two branches of the band which is unsymmetrical and disagrees with the experimental observations. The theoretical intensity (i.e. integral absorption coefficient) of the first line of the positive branch is more than twice that of the first line of the negative branch. This dissymmetry may be greatly reduced if the a priori probability of the upper quantum level, which appears as a factor in the intensity formula, is replaced by the mean of the a priori probabilities of the initial and final states. Such a modification of the theory is justified by a recalculation of intensities, *treating the molecule as a non-degenerate system*, e.g., one whose orbits are quantized in space under the influence of a weak magnetic field. A comparison between the theory and experiment involves the computation of the total absorptions to be expected in a tube of appreciable length using a relatively wide slit. If this computation is based on the assumption that the lines have no unresolved fine structure, the estimated absorptions do not agree with experiment, but the assumption that such a fine structure does exist, combined with the integral absorption coefficients of the modified theory, gives fair agreement with the available observations. *General theory of transition probabilities.* It is pointed out that the usual method of calculating probabilities involves a discontinuity in the intensities of spectrum lines when a degenerate system is converted into a non-degenerate one, as by a weak magnetic field. This seems improbable and the failure of the first calculation indicates that the usual rules for the treatment of degenerate systems require modification.

* This article is essentially an expansion of a note published in the Proceedings of the National Academy of Science, 10, 274 (June 1924)

Introduction

THE characteristic feature of infra-red absorption bands on which Bjerrum based his well-known theory was the doublet structure as observed with a spectroscope of moderate resolving power. This structure, so similar to that to be expected on a purely classical basis from the compounding of molecular vibrations and rotations, is essentially an intensity distribution due, as Bjerrum supposed, to differences in the numbers of molecules effective in producing absorption in different parts of the band. The graph of the absorption coefficient plotted against frequency was concieved by him to be a doubled and somewhat distorted Maxwell distribution law curve for angular velocities. This hypothesis made possible the calculation of the molecular moments of inertia of diatomic gases from the spacing of the maxima of their absorption doublets. When the fine structure of the halogen hydride bands was discovered, it was assumed that the intensity of each component line was a measure of the number of molecules in the corresponding absorbing state and the theoretical relation between the doublet spacing of the gross structure and the molecular moment of inertia remained as before.[1] A comparison of the values of the moment of inertia of HCl obtained from the fine structure and from the gross structure gave one of the earliest important checks on the theory.

This simple view of the relative intensities of band components has been retained since the introduction of Bohr's hypotheses into band spectrum theory, but finally breaks down with the reinterpretation of the structure of the bands of the halogen hydrides in terms of half integral quantum numbers first suggested by Kratzer[2] and more recently confirmed by Colby.[3] In fact the writer in a paper read before the American Physical Society in April 1923,[4] opposed the application of the "half quantum" idea to the bands in question because of its apparent conflict with the observed distribution of intensities among their components.

This conflict will be readily understood by reference to Figs. 1 and 2 which show the well-known absorption curve for the HCl band at 3.5μ as observed by Imes[5] and by Brinsmade and Kemble.[6] The high frequency (positive) branch is supposed to be due to molecules which

[1] Cf. N. Bjerrum, Verh. d. Deutsch. Phys. Ges. **16**, 640 (1914);
E. C. Kemble, Phys. Rev. **8**, 689 (1916)
[2] A. Kratzer, Münchener Akad. p. 107 (1922)
[3] W. Colby, Astrophys. J. **58**, 303 (1923)
[4] E. C. Kemble, Phys. Rev. **21**, 713 (1923)
[5] E. S. Imes, Astrophys, J. **50**, 260 (1919)
[6] J B. Brinsmade and E. C. Kemble, Proc. Nat. Acad. Sci. **3**, 420 (1917)

pick up a unit of angular momentum as they absorb vibrational energy, while the low frequency (negative) branch is produced by molecules which drop a unit of angular momentum in the process of absorption. The numbers on the lines in Fig. 1 show the rotational quantum numbers assigned in Kratzer's earlier theory to the associated initial states. The approximate equality of corresponding components of the positive and negative branches fits very well with this assignment of quantum numbers and the hypothesis that the intensity of an absorption component depends primarily on the initial state. But according to Kratzer's new theory, corresponding components of the positive and negative branches have neither the same initial state nor the same final state and hence should not have equal intensities. To be explicit, let us introduce the symbol (n, m) to denote the state of a molecule having the vibrational

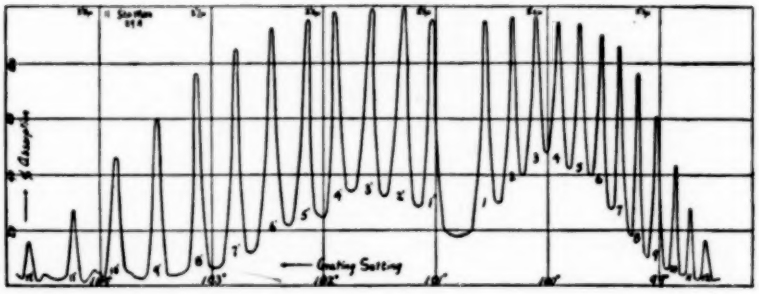

Fig. 1. The HCl band at 3.46μ, mapped with 7500-line grating; HCl at atmospheric pressure (Imes, Astrophysical Journal, **50**, 260, 1919).

quantum number n and the nuclear angular momentum $mh/2\pi$. The first component of the positive branch is attributed by the new theory to the jump $(0, \frac{1}{2})\rightarrow(1, 3/2)$, while the first component of the negative branch is supposed to result from the jump $(0, 3/2)\rightarrow(1, \frac{1}{2})$. The a priori probability of the initial state for the former of these two lines is half that for the latter and it can readily be shown that the number of molecules in it is not much more than half as great. In the writer's opinion the evidence from the combination principle brought forward by Colby in favor of the new assignment of quantum numbers is conclusive. We are therefore confronted with a sharp disagreement between the early simple theory of intensities and the experimental observations shown in Figs. 1 and 2.

The same difficulty is met in the study of electronic emission bands.[7] For example, the first components of the positive and negative branches

[7] The writer is indebted to Prof. R. T. Birge for information on this point.

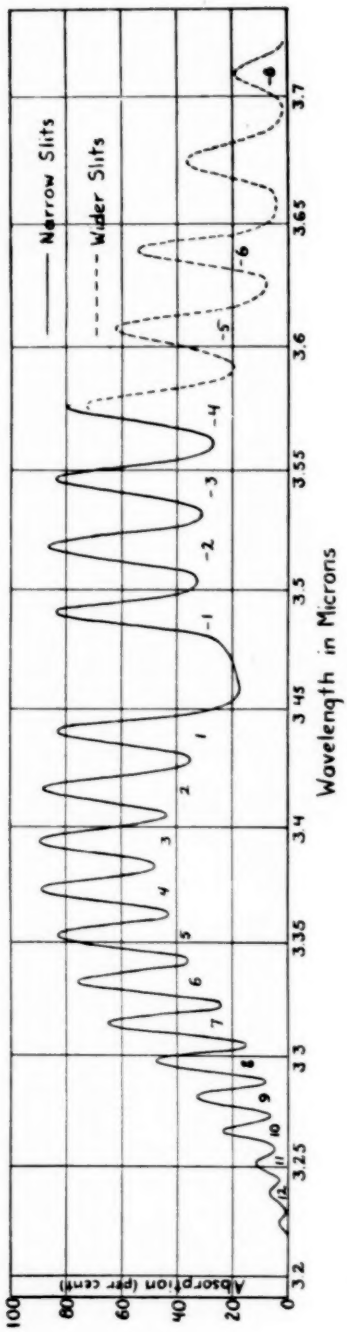

Fig. 2.

of the "cyanogen" band λ3383 A are of approximately equal intensity though neither the inital nor final rotational quantum numbers are the same for these two lines. Moreover, it follows from Kirchhoff's law that if the intensities of two absorption lines are proportional to the a priori probabilities of the initial states, the intensities of the same lines in emission must be proportional to the a priori probabilities of the corresponding final states—a conclusion of an unsatisfactory character.

The purpose of this paper is to study the problem from the standpoint of Bohr's correspondence principle. In the first part of the paper the intensities of the lines in the infra-red absorption spectrum of a diatomic gas will be calculated theoretically treating the molecule in the usual way as a degenerate system with but one quantum condition for two rotational degrees of freedom. The computed intensities are neither proportional to the numbers of molecules in the initial states[5] nor are they in agreement with the experimental observations. In the second part of the paper the intensities are recomputed assuming the existence of a slight precessional motion of the planes of rotation about the lines of the earth's magnetic field and space quantization of these planes. The recomputed intensities are in fair agree-

[5] Contrary to the writer's earlier statement.[4]

ment with the experimental facts. In the writer's opinion the neutralization of the earth's magnetic field would probably not produce any great change in the actual relative intensities of the lines, so that the success of the second calculation is not to be interpreted as a proof of the reality of the assumed space quantization but points to the necessity of modifying the usual method of applying the correspondence principle to degenerate systems.

General Theory of the Intensities of Absorption Lines

Consider the absorption line due to jumps from the initial state (n'', m'') to the final state (n', m'). (The double prime will always denote the state of lower energy whether the discussion relates to absorption or emission.) Let N'' be the number of molecules in the initial state. Let u_ν denote the volume density of the radiant energy of frequency ν in the radiation field. In his basic derivation of the black body radiation formula Einstein treats u_ν as constant across the absorption line and sets the energy absorbed per unit volume per unit time equal to

$$N''B''_{,}u_\nu h\nu. \tag{1}$$

$B''_{,}$ denotes a numerical coefficient which gives the probability that any individual molecule in the initial state will make the transition in a unit time, and h is Planck's constant. If the symbol α_ν is introduced for the coefficient of absorption of the gas for light of frequency ν, the rate of absorption of energy per unit volume is readily shown to be

$$cu_\nu \int \alpha_\nu d\nu \tag{2}$$

where c is the velocity of light and the integration is carried over the width of the absorption line. It is convenient to introduce the symbol $\alpha''_{,}$ for the integral absorption coefficient $\int \alpha_\nu d\nu$. (This quantity is to be identified with the rather vague term "intensity of an absorption line" used in the introduction.) Equating the expressions (1) and (2) and solving for $\alpha''_{,}$ we get the fundamental relation

$$\alpha''_{,} = (h\nu/c)N''B''_{,}. \tag{3}$$

If the intensity of the beam of radiation used in the absorption measurements is not so great as to affect appreciably the relative numbers of molecules in the stationary states, we may introduce the usual statistical formula for N'' in terms of the temperature T, the energy W'', and the a priori probability p''. Eq. (3) takes the form

$$\alpha''_{,} = C\nu p'' e^{-W''/kT} B''_{,} \tag{4}$$

in which C depends only on the temperature and the nature of the gas.

Einstein[9] has shown that $B'_{,''}$ is related to the probability coefficient $A'_{,,}$ for emission by spontaneous transition from the state (n', m') to the state (n'', m'') by the formula

$$B'_{,''} = \frac{c^3}{8\pi h\nu^3} \frac{p' A'_{,,}}{p''} . \tag{5}$$

The expression for the integral absorption coefficient in terms of $A_{,,}$ is therefore

$$\alpha'_{,''} = (C_1 p'/\nu^2) e^{-W''/kT} A'_{,,} . \tag{6}$$

APPLICATION OF BOHR'S CORRESPONDENCE PRINCIPLE: SYSTEM TREATED AS DEGENERATE.

In order to determine $A'_{,,}$ and $\alpha_{,}'$ theoretically, we use Bohr's correspondence principle. Let M_x, M_y, M_z denote the directional components of the electric moment of the molecule. Let X, Y, Z denote the respective amplitudes of the Fourier series components of M_x, M_y, M_z correlated in the usual way with the transition or "jump" which gives rise to the absorption and emission line under discussion. Each of these amplitudes depends on the particular "orbit" or motion for which it is worked out. The choice of orbit actually under consideration is conveniently indicated by its quantum numbers n and m. (In order to include in the discussion hypothetical non-quantized orbits between the initial and final states, it is convenient to define each of the quantum numbers as $1/h$ times the corresponding phase integral whatever its value may be). X, Y, Z are then functions of n and m. According to Kramers[10]

$$A_{,,} = (16\pi^4\nu^3/3hc^3)\,\overline{(X^2+Y^2+Z^2)}, \tag{7}$$

where the sum of the squares of the amplitudes is to be averaged over the hypothetical classical orbits between the initial and final states of the molecule. The method of averaging is uncertain, and, in fact, it is uncertain whether any definite scheme of averaging will always give rigorous results. Kramers has used the simple approximate assumption that X^2 is equal to the mean of the values of X^2 for the initial and final orbits. Other possibilities have recently been discussed by Hoyt.[11] The method of averaging is not important for the present purpose since the

[9] A. Einstein, Phys. Zeits. **18**, 121 (1917)

[10] H. A. Kramers, Kgl. Danske Vidensk Selsk. Skrifter 8, Raekke III, 330 (1919). See also reference 11, equation (1).

[11] F. C. Hoyt, Phil. Mag. **47**, 826 (1924)

amplitudes are not greatly affected by a small change in m and since the variation of amplitude with the vibrational quantum number n does not affect the relative intensities of the lines in any single band. (We shall not attempt to discuss the relative intensities of the different bands in a system.) It has therefore seemed permissible to identify the mean values of X^2, Y^2, Z^2 with the values of these quantities for the intermediate orbit n,m whose quantum numbers are the averages of the values of n and m for the actual initial and final orbits. Using this assumption we rewrite (6) as follows:

$$a_{\tau}'' = C_{2\nu} p' e^{-W''/kT} [X^2(\bar{n}, \bar{m}) + Y^2(\bar{n}, \bar{m}) + Z^2(\bar{n}, \bar{m})] . \qquad (8)$$

The electric moment of the molecule is assumed to be proportional to the vector distance between the atomic nuclei. Neglecting for the present any possible precession about lines of magnetic force and assuming a non-gyroscopic molecular model, it is clear that the motion of the terminal point of the vector M must be uniplanar and compounded of a vibration whose frequency we denote by ω_v and a rotation whose frequency we denote by ω_r. To determine X, Y, and Z we have to resolve M into components along three fixed axes and then analyze each component into Fourier series. The analysis is similar to that given by Sommerfeld and Heisenberg in their article on "The Intensity of Multiple Lines and their Zeeman Components."[12] It is convenient to introduce two sets of axes x, y, z and x', y', z' with a common origin. The first set is fixed in space, the xy plane being the plane of the orbit. The z' axis of the second set coincides with the z axis of the first and the $x'y'$ plane coincides with the xy plane, but the $x'y'$ axes rotate with constant angular velocity $2\pi\omega_r$ about the z axis. The sense of this rotation being the same as that of the molecule, it is evident that the orbit of the terminal point of M referred to the $x'y'$ axes is closed and periodic. If the molecular rotation took place at a uniform rate, the orbit would degenerate into a straight radial line, but owing to the variation in angular velocity with the radial vibrations of the molecule, it is actually of an elongated oval form as indicated in Fig. 3. Since the angular velocity of the molecule has its greatest value when the atoms are closest together, it is clear that the sense of the precession of the x' y' axes is opposite to the sense of rotation on the closed orbit in the x' y' plane.

The Fourier development is conveniently written in the complex form

$$M_{x'} + iM_{y'} = \sum_{\tau=0}^{\tau=\infty} [R_\tau e^{2\pi i(\tau\omega_v t+\delta)} + R_\tau' e^{-2\pi i(\tau\omega_v t-\delta)}] \cdot \tau = 0,\ 1,\ 2,\ \ldots \qquad (9)$$

[12] A. Sommerfeld and W. Heisenberg, Zeits. f. Phys. 11, 131 (1922)

R^τ, $R^{\tau\prime}$, and δ denote real constants. Shifting to fixed axes is equivalent to multiplying by $e^{2\pi i\omega t}$ so that

$$M_x+iM_y=\sum_{\tau=0}^{\tau=\infty}[R_\tau e^{2\pi i[(\tau\omega_v+\omega_r)t+\delta]}+R_\tau' e^{-2\pi i[(\tau\omega_v-\omega_r)t-\delta]}]\cdot\tau=0,\ 1,\ 2, \quad (10)$$

Each of the infra-red absorption bands of a diatomic gas is correlated with some particular value of τ. The positive branch of the band is associated with the classical Fourier component whose frequency is $\tau\omega_v+\omega_r$ while the negative branch is associated with the component of

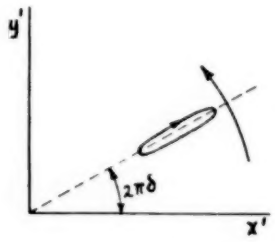

Fig. 3.

frequency $\tau\omega_v-\omega_r$. The relative probabilities of the transitions which give rise to the positive and negative branches of the band are therefore bound up with the relative values of R_τ and R_τ' respectively. The ratio of these coefficients depends in turn on the eccentricity of the orbit in the $x'y'$ plane. If this orbit is treated in first approximation as a radial straight line, these coefficients are equal. An exact determination of their values would be difficult and would require a specific assumption regarding the law of force governing the radial vibrations of the molecule. Without such an assumption, however, a second approximation valid for the coefficients R_τ and R_τ' of the important "fundamental" vibration-rotation band[13] may be carried through. It leads to the formulas

$$R_1=A\left(\frac{\omega_v}{\omega_v+\omega_r}\right)^2;\qquad R_1'=A\left(\frac{\omega_v}{\omega_v-\omega_r}\right)^2. \quad (11)$$

The proof of these equations is given in the supplement to this paper. Further approximations hardly seemed justified at present. The amplitude A and the frequency ω_v in the above formulas vary slightly with the rotational quantum number of the orbit for which they are evaluated, but the variations in these quantities may be neglected in comparison with the large variations in ω_r.

[13] See Supplementary Note at end of this paper.

It follows from the correspondence principle and Eq. (10) that R_τ and R_τ' are the amplitudes of the Fourier components of M_x and M_y corresponding to the transition groups for which $\Delta n = \tau$, $\Delta m = +1$, and $\Delta n = \tau$, $\Delta m = -1$, respectively.[14] The frequency ν absorbed in any given transition of the former class (positive branch) is the mean value of $\tau\omega_v + \omega_r$ taken over all orbits between the initial and final states, while the frequency absorbed in any given transition of the latter class (negative branch) is the corresponding mean value of $\tau\omega_v - \omega_r$. Hence Eqs. (11), translated into the notation of Eqs. (7) and (8), yield

$$X_1 = Y_1 = \text{Const.}/\nu^2; \qquad Z_1 = 0. \tag{12}$$

Eq. (8) specialized for the "fundamental" vibration-rotation band now becomes

$$a_r'' = \text{Const.}\,(p'/\nu^3)e^{-W''/kT}. \tag{13}$$

The approximations involved in Eqs. (12) and (13) are based on the assumption that ω_r is small compared with ω_v. This assumption is least accurate for the outer members of the band and Eq. (13) should be applied to them with caution.

Comparison of Theory and Experiment

The above equation gives the relative intensities of the various components of the fundamental vibration-rotation band as required by the Bohr correspondence principle in the form hitherto accepted. It asserts that the relative intensity of any line is fixed by the product of three factors of which one is determined by the position of the line in the spectrum, another depends on the final state of the absorbing molecule (upper energy level), while the third depends on the initial state. The first factor $1/\nu^3$, due to the ellipticity of the orbit when referred to the rotating $x'y'$ axes, tends to make the outer components of the negative branch more intense than those of the positive branch. In the case of the HCl band shown in Figs. 1 and 2 the values of $1/\nu^3$ for the outermost components ($+12$ and -12) differ by about fifty per cent. This factor is of little importance in fixing the ratio of the intensities of neighboring lines. The second factor p' is the a priori probability of the upper energy level and is probably equal to $2m'+1$.[15] This factor tends to make the outer

[14] Δn and Δm denote the increments in n and m respectively for the absorption process.

[15] Specific heat calculations for H_2 using the old integral rotational quantum numbers favor the use of the formula $p_m = 2m$ (see Kemble and Van Vleck, Phys. Rev. **21**, 657-659, 1923), but the computations of R. C. Tolman (Phys. Rev. **22**, 470, 1923) based on half-integral quantum numbers favor the formula $p_m = 2m+1$. The latter formula

components of both branches more intense than the inner ones. The exponential factor works in just the opposite way to p'. Fig. 4, Curve *a*, shows diagrammatically the integral absorption coefficients of the lines in the HCl band at 3.46μ as computed by Eq. (13) assuming

$$p' = 2m' + 1 \qquad m' = \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \ldots \qquad (14)$$

The values of w'' were computed from the formula

$$W'' = 10.46hc(m'')^2 \qquad m'' = \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \ldots$$

which is based on Colby's frequency measurements. The temperature of the gas in this and later computations is taken to be 293°K.

Curve *b* of Fig. 4 shows the effect on the computed intensities of arbitrarily replacing the factor p' by p'', thus making the absorption proportional to the number of molecules in the initial state.

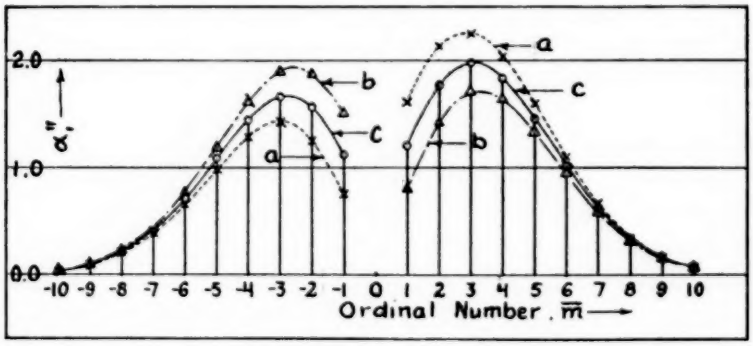

Fig. 4.

In comparing these graphs with the experimental curves of Figs. 1 and 2 the reader should bear in mind that the latter show total absorptions and not absorption coefficients, so that the intensity differences in them are to a large extent "ironed out." The differences between the two experimental curves, due largely to differences in slit width and tube length, are so considerable that close agreement with the theoretical curves is not to be expected. There is a marked discrepancy at the center of the band, however, which clearly shows that neither theoretical curve can be right. In curve *a* the high frequency branch is relatively much more intense than the low frequency branch, especially near the center, while in curve *b* the difference is reversed. In the measurements of Brinsmade and Kemble (Fig. 2) particular care was taken to observe

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is in accord with Heisenberg's assumption that the magnetic quantum numbers for "doublet" atoms should have the values $\pm(1/2, 3/2, 5/2, \ldots)$ (see W. Heisenberg, Zeits. f. Phys. **8**, 273 (1922).

the relative heights of the first maxima to the right and left of the center. They were very nearly equal, so that the experimental data are incompatible with both theories.

Remarks on the General Problem of Emission and Absorption by a Degenerate Molecular System

In view of the above discrepancy it is appropriate to re-examine the general problem of the intensities of absorption and emission lines in a degenerate system where the a priori probabilities of the initial and final states are not necessarily the same. Such a degenerate system, as is well known, may frequently be reduced to a non-degenerate one by the application of an external force field which resolves each of the original stationary states into a group of subsidiary states. The subsidiary states are equally probable and the number of such states in each group is equal to the a priori probability of the initial stationary state. In this case each of the original spectrum lines is resolved into a group of closely spaced components the intensities of which are calculable in theory as before. The new computations are simpler, however, and perhaps more certain, since the a priori probabilities of the various states, being equal, drop out of consideration. It seems to the writer altogether probable that the sum of the intensities of the group of lines produced by the external field will continuously approach the intensity of the parent line as the field approaches zero. This assumption will be called the hypothesis of the continuity of intensities. It makes possible the calculation of the intensities of emission or absorption lines due to a degenerate system in a new indirect way. It is supported by the fact that according to the classical electromagnetic theory no sudden change in intensity would be produced by an incipient external field, and also by the result of the calculations of the next section, but it is in conflict with the formulation of the correspondence principle by Kramers.

In order to see just how this formula disagrees with the hypothesis of the continuity of intensities, let us consider the radiation emitted as a result of a transition between two degenerate states S' and S''. It requires that the rate of spontaneous emission of radiation be proportional to $\nu^4 N'(\overline{X^2+Y^2+Z^2})$. If a small external field is applied so that the upper energy level S' is broken up into p' subsidiary levels and the lower level into p'' subsidiary levels the combined rate of spontaneous emission due to all transitions from the upper group to the lower group is proportional to an expression of the form $\Sigma(k=1 \text{ to } p_1') \Sigma(l=1 \text{ to } p'') \nu_{kl}^4 N_k (\overline{X_{kl}^2+Y_{kl}^2+Z_{kl}^2})$. Hence the hypothesis of the continuity

of the intensities can harmonize with Kramers' theory only if, in the limit when the field is very small,

$$\nu^4 N'\overline{(X^2+Y^2+Z^2)} = \sum_{k=1}^{k=p'} \sum_{l=1}^{l=p''} \nu_{kl}^4 N_k \overline{(X_{kl}^2+Y_{kl}^2+Z_{kl}^2)} \,. \tag{15}$$

Introducing the statistical formulas for N' and the various N_k's and cancelling common factors, we reduce the above equation to the form

$$p'\overline{(X^2+Y^2+Z^2)} = \sum_{k=1}^{k=p'} \sum_{l=1}^{l=p''} \overline{(X_{kl}^2+Y_{kl}^2+Z_{kl}^2)} \,. \tag{16}$$

The right hand member of (16) is symmetrically related to the a priori probabilities p' and p'' of the initial and final states, while the left hand member is unsymmetrical. The equation therefore must be incorrect, and either the assumption of continuous intensities or Eq. (7) must be given up.* In the next section we proceed to a recalculation of the relative intensities of band lines based on Kramers' theory for non-degenerate systems and on the hypothesis of the continuity of intensities.

Application of Bohr Correspondence Principle: System treated as Non-Degenerate

If the resultant intensity of a group of related lines produced by a small external field is sensibly the same as that of the single line into which they merge when the field is absent, it is clear that the resultant intensity must be independent of the exact nature of the external field and of the manner in which the degenerate system is made non-degenerate. In the absence of a satisfactory theory of the Zeeman effect for bands it seems plausible, therefore, to proceed with a formal application of the method of "spatial quantization" used in the theory of the Zeeman effect for hydrogen atoms. We assume that the component of the angular momentum parallel to the field is $rh/2\pi$, where r is the magnetic quantum number. We further

* Note added at time of reading proof: Since writing this paper the author's attention has been called to the fact that in his dissertation[10] Kramers observed the existence of a discrepancy in the intensities of the fine structure components of the H and He^+ lines (a) computed directly, treating the system as degenerate, and (b) computed indirectly from the Zeeman analysis. He did not follow up the point, however, nor did he indicate which method was to be preferred.

Kramers also compared the intensities of the fine structure lines in the spectrum of He with the values of the product of a priori probability and square of amplitude worked out for the final state as well as the initial, thus showing that he clearly recognized the possibility that the a priori probability of the final state might have an influence on the probability of transition.

suppose that for any given m, r takes on the values $\pm 1/2$, $\pm 3/2$, . . . $\pm m$.[16]

Associated with the magnetic quantum number r is a slight precessional motion of the orbital plane, of frequency σ. To get the new Fourier development the x, y, z system of axes previously considered may be supposed to rotate with constant angular velocity $2\pi\sigma$ about the lines of magnetic force. Let ξ, η, ζ be a new set of fixed axes so chosen that ζ coincides with the field. Let θ denote the constant angle between z and ζ. Without loss of generality we may assume that the x-axis lies in the ξ,η plane and makes an angle $2\pi\sigma t$ with the ξ axis. Shifting to the new axes we use the transformation equations

$$M_\xi + iM_\eta = \left\{ \tfrac{1}{2}(1+\cos\theta)\,(M_x + iM_y) + \tfrac{1}{2}(1-\cos\theta)(M_x - iM_y) \right\} e^{2\pi i\sigma t} ; \quad (17)$$

$$M_\zeta = M_y \sin\theta .$$

Hence

$$\begin{aligned} M_\xi + iM_\eta = {} & \tfrac{1}{2}(1+\cos\theta)\left\{ Re^{2\pi i\left\{(\omega_v+\omega_r+\sigma)t+\delta\right\}} + R'e^{-2\pi i\left\{(\omega_v-\omega_r-\sigma)t-\delta\right\}} \right\} \\ & + \tfrac{1}{2}(1-\cos\theta)\left\{ Re^{-2\pi i\left\{(\omega_v+\omega_r-\sigma)t+\delta\right\}} + R'e^{2\pi i\left\{(\omega_v-\omega_r+\sigma)t-\delta\right\}} \right\} \quad (18) \\ M_\zeta = {} & \sin\theta\left[R\sin\left\{2\pi(\omega_v+\omega_r)t+\delta\right\} - R'\sin\left\{2\pi(\omega_v-\omega_r)t-\delta\right\} \right] . \end{aligned}$$

The coefficients ± 1, 0 of ω_r and σ in the development give the values of Δm and Δr for the transitions with which the terms in the Fourier series are associated. Let $\Xi_{\Delta r}^{\Delta m}(\bar{m}, \bar{r})$, $\mathrm{H}_{\Delta r}^{\Delta m}(\bar{m}, \bar{r})$, $\mathrm{Z}_{\Delta r}^{\Delta m}(\bar{m}, \bar{r})$ be the ξ, η, ζ components of the amplitudes evaluated for the mean orbit $\bar{m}, \bar{r}$. Then, since $\cos\theta = r/m$,

$$\begin{aligned} & \Xi_{+1}^{+1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R(1+\bar{r}/\bar{m}) ; \qquad \Xi_{-1}^{+1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R(1-\bar{r}/\bar{m}) ; \\ & \Xi_{+1}^{-1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R'(1-\bar{r}/\bar{m}) ; \qquad \Xi_{-1}^{-1}(\bar{m}, \bar{r}) = \tfrac{1}{2}R'(1+\bar{r}/\bar{m}) ; \\ & \mathrm{H}_{\Delta r}^{\Delta m}(\bar{m}, \bar{r}) = \Xi_{\Delta r}^{\Delta m}(\bar{m}, \bar{r}) ; \\ & \mathrm{Z}_{0}^{+1}(\bar{m}, \bar{r}) = R\sin\bar{\theta} = R\sqrt{1-(\bar{r}/\bar{m})^2} ; \quad \mathrm{Z}_{0}^{-1}(\bar{m}, \bar{r}) = R'\sqrt{1-(\bar{r}/\bar{m})^2} \end{aligned} \quad (19)$$

All other coefficients vanish.

[16] In accordance with Heisenberg's hypothesis as mentioned above[15].

The absorption intensity of one of the fine structure components is to be obtained from an equation of the form of (8) with p' set equal to unity and appropriate values of Ξ, H, Z replacing X, Y, Z. To get the total absorption intensity of a group of magnetic components we have to sum up over all values of $\bar{r}$ and Δr consistent with the values of $\bar{m}$ and Δm under consideration. As the discussion is restricted to a definite pair of values of n' and n'' and as ± 1 are the only values of Δm to be considered, it is convenient to modify the notation for the absorption

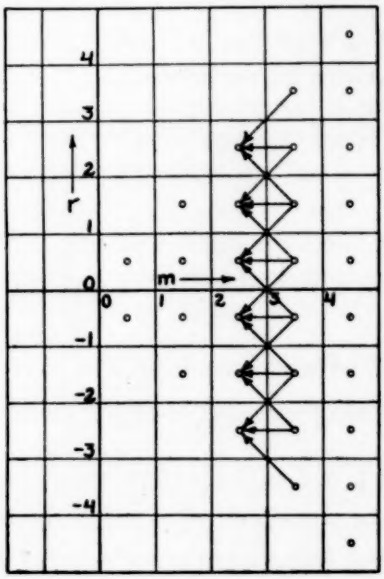

Fig. 5.

coefficients. Let $a^+(\bar{m})$ denote the integral absorption coefficient for the component of the high frequency branch ($\Delta m = +1$) having the mean rotational quantum number $\bar{m}$. Let $a^-(\bar{m})$ denote the coefficient for the component of the negative branch having the same mean rotational quantum number. Then

$$a^+(\bar{m}) = \text{Const.} \times \nu R^2 \sum_{\bar{r}} \left\{ \tfrac{1}{2}(1+\bar{r}/\bar{m})^2 + \tfrac{1}{2}(1-\bar{r}/\bar{m})^2 + 1 - (\bar{r}/\bar{m})^2 \right\} e^{-W''/kT}$$

$$a^-(\bar{m}) = \text{Const.} \times \nu R'^2 \sum_{\bar{r}} \left\{ \tfrac{1}{2}(1+\bar{r}/\bar{m})^2 + \tfrac{1}{2}(1-\bar{r}/\bar{m})^2 + 1 - (\bar{r}/\bar{m})^2 \right\} e^{-W''/kT} \tag{20}$$

Let $2S(\bar{m})$ denote the sum which appears in each of the above equations. Introducing the values previously obtained for R_1 and R_1' (thereby

restricting the discussion as before to the fundamental band of the infra-red system) we condense (20) into the form

$$a^{\pm}(\bar{m}) = \text{Const.} \times [S(\bar{m})/\nu^3] e^{-W''/kT}. \tag{21}$$

In evaluating $S(\bar{m})$ it is convenient to make use of Fig. 5 in which r and m are laid out as ordinate and abscissa respectively. The circles

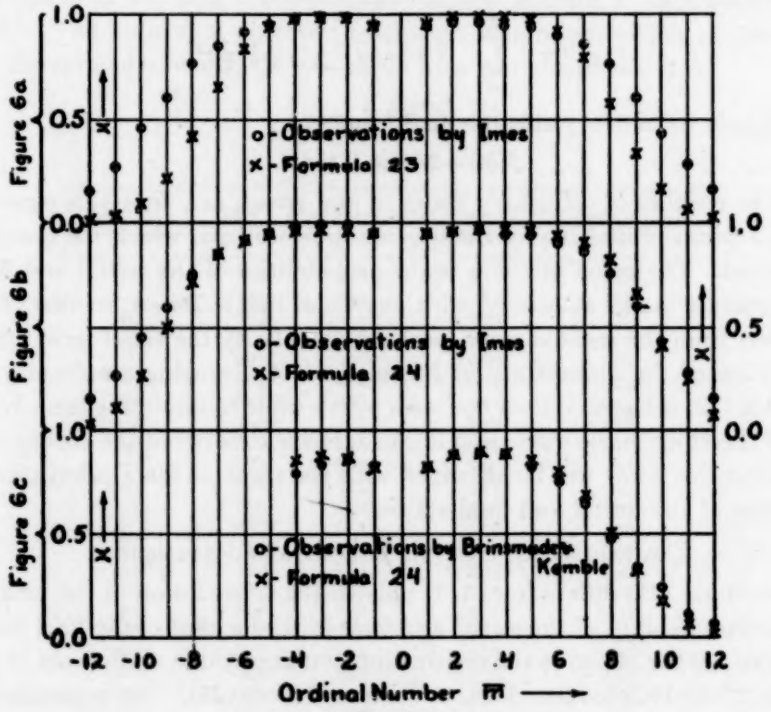

Fig. 6.

indicate the r,m values of the assumed stationary states and the full arrows show a set of emission transitions giving rise to the third line in the positive branch of the band. The initial and final vibrational quantum numbers cannot be shown in two dimensions, but this incompleteness does not seriously detract from the value of the diagram.

The subgroup of transitions for which $\Delta r = 0$ is shown by horizontal arrows. This subgroup gives rise to the term $[1-(\bar{r}/\bar{m})^2]$ in equations (20) and is to be summed from $\bar{r} = -(\bar{m}-\frac{1}{2})$ to $\bar{r} = +(\bar{m}-\frac{1}{2})$. The subgroup of transitions for which $\Delta r = +1$ is shown by downward pointing arrows (cf. note[14]). The term $\frac{1}{2}(1+\bar{r}/\bar{m})^2$ with which this second subgroup of transitions is correlated should be summed from $\bar{r} = -(\bar{m}-1)$

to $\bar{r}=\bar{m}$ according to the diagram, but since the added term is zero, we may formally sum from $-\bar{m}$ to $+\bar{m}$. Similarly the subgroup of transitions for which $\Delta r=-1$ yields the term $\frac{1}{2}(1-\bar{r}/\bar{m})^2$ which may be summed from $\bar{r}=-\bar{m}$ to $r=+m$. Hence

$$2S(\bar{m})=\sum_{\tau=-\bar{m}}^{\tau=+\bar{m}}\left[1+(\tau/\bar{m})^2\right]+\sum_{\tau=-(\bar{m}-\frac{1}{2})}^{\tau=+(\bar{m}-\frac{1}{2})}\left[1-(\tau/\bar{m})^2\right]$$

$$=1+2\sum_{\tau=1}^{\bar{m}}\left[2+(\tau/\bar{m})^2-(\tau-\tfrac{1}{2}/\bar{m})^2\right].$$

A simple reduction yields the final formula

$$S(\bar{m})=2\bar{m}+1-1/4\bar{m}. \tag{22}$$

The number of subsidiary states in any group, i.e., $2m+1$, is equal to the a priori probability of the degenerate state from which the group is derived. The mean of the a priori probabilities of the initial and final degenerate states associated with any band line is $2\bar{m}+1$, so that $S(\bar{m})$ differs from the mean a priori probability only by the small term $1/4\bar{m}$. In view of the uncertainty of the method of averaging amplitudes on which (22) is based, it does not seem worth while to retain the term $1/4\bar{m}$ and therefore in the discussion of the agreement between the theory and experiment, $S(\bar{m})$ will be identified with the mean of the a priori probabilities of the initial and final states.

Comparison of Second Theory and Experiment

Formula (21) differs from (13) only in the substitution of the mean a priori probability of the initial and final states for that of the final state. Curve *c* of Fig. 4 shows the relative integral absorption coefficients of the lines of the HCl band at 3.46μ as computed from (21). The intensities of the central components of the two branches are much more nearly the same, and, though the symmetry is less perfect than Fig. 1 would suggest, the discrepancies between the theory and experiment are much less serious than before.

In order to see more clearly just how important the discrepancies are, the writer has attempted to compute from the theoretical integral absorption coefficients a corresponding set of maximum total absorptions directly comparable with the absorption maxima of Figs. 1 and 2. Such a calculation is admittedly crude and serves merely to show that Eqs. (21) and (22) are not incompatible with the experimental data now available. The final test of the theory can only come after conclusive experimental measurements of the integral absorption coefficients have been made.

The computation of total absorptions is based on the assumption that the different lines are of the same breadth and structure so that the maximum absorption coefficients are in the same ratio as the integral absorption coefficients. A preliminary set of calculations was made on the hypothesis that the lines have no unresolved fine structure and that the radiation entering the slit of the receiving thermopile when set on the center of any individual line has a single definite absorption coefficient. The maximum observed fractional absorption, which we denote by the symbol κ, would then be given by a formula of the type

$$\kappa = 1 - e^{-a a_m''} \tag{23}$$

TABLE I

Ordinal number m	a_m'' (Eq. 21)	Maximum fractional total absorption κ (Eq. 23)	(Eq. 24)	Imes
+1	1.206	.950	.951	.948
−1	1.136	.941	.947	.950
+2	1.782	.988	.966	.958
−2	1.571	.980	.962	.992
+3	1.991	.993	.970	.961
−3	1.672	.984	.964	.990
+4	1.845	.990	.967	.945
−4	1.456	.973	.959	.976
+5	1.469	.974	.959	.940
−5	1.094	.934	.945	.951
+6	1.025	.922	.941	.900
−6	.718	.832	.916	.921
+7	.630	.791	.905	.858
−7	.415	.643	.856	.849
+8	.342	.573	.825	.763
−8	.212	.409	.725	.760
+9	.166	.338	.661	.605
−9	.097	.215	.505	.600
+10	.072	.164	.419	.433
−10	.040	.095	.270	.460
+11	.028	.068	.252	.280
−11	.0145	.035	.111	.273
+12	.010	.024	.074	.163
−12	.005	.012	.038	.156

in which a is a quantity the same for all the lines in the band but varying with the length of the absorption tube and the pressure of the absorbing gas. Table I and Fig. 6*a* show the result of the calculation. The circles in the figure show the experimental absorptions taken from Imes' curve and the crosses show the theoretical absorptions based on (23) after adjusting the constant a to give the best possible agreement for the central pair of lines. The marked discrepancies for the outer lines suggest that the exponential law of absorption does not apply. This result was anticipated in view of the doubling of the lines in the first harmonic band by the isotope effect.

A second set of calculations was therefore carried through on the hypothesis that the radiation entering the thermopile slit is uniformly distributed across a small frequency interval in which the coefficient of absorption a_ν varies linearly between zero and a maximum value ga_ν''. This assumption is merely a rough guess made to show in a general way the effect of an unresolved fine structure on the total absorption. If I_0 is the initial intensity of the beam of radiation and I the intensity after traversing a depth x of absorbing gas, we have

$$I = I_0 \int_0^{ga_\nu''} e^{-a_\nu x} da_\nu = I_0 \left(\frac{1 - e^{-ga_\nu'' x}}{ga_\nu'' x} \right).$$

The fractional total absorption is therefore

$$\kappa = \frac{I - I_0}{I_0} = 1 - \left(\frac{1 - e^{-aa_\nu''}}{aa_\nu''} \right), \tag{24}$$

where a is a new symbol for the product gx. The result of the calculation is shown in Table I and by Fig. 6b. As in Fig. 6a the circles show experimental values and the crosses the theoretical ones. Table II and Fig. 6c show the result of a similar attempt to fit the observations of Brinsmade and Kemble (Fig. 2) by means of formulas (21) and (24).

TABLE II

$\bar{m}$	κ (Eq. 24)	κ (Brinsmade and Kemble)
+1	.831	.825
−1	.822	.835
+2	.886	.884
−2	.870	.863
+3	.897	.891
−3	.878	.835
+4	.890	.886
−4	.860	.793
+5	.861	.826
−5	.814	
+6	.802	.756
−6	.724	
+7	.690	.647
−7	.572	
+8	.515	.474
−8	.379	
+9	.316	.330
−9		
+10	.158	.234
−10		
+11	.062	.280
−11		
+12	.020	.156

In view of the uncertainty regarding the relation between the fractional total absorption and the integral absorption coefficient and of the discrepancies between the two sets of observations shown in Figs. 1 and 2, the agreement between the computed values and the theoretical data seems to the writer fairly satisfactory. He is therefore of the opinion that the hypothesis of the continuity of intensities under the influence of a small perturbing field gives an acceptable way out of the impasse into which we are led by the direct application of equation (7) to the transitions of the degenerate diatomic molecule. The problem of reformulating a method of calculating the probabilities of transition for a degenerate system so as to conform to the new principle of continuity has yet to be solved.

Remarks on the Structure of the Lines of the HCl Infra-red Bands

The theory developed above had its origin in an attempt to harmonize the Kratzer half integral quantum numbers with the observed symmetry in the intensities of the positive and negative branches of the HCl band at 3.46μ. A related source of difficulty to which the writer called attention in the paper cited above[4] arises from the fact that according to Kratzer all of the lines except the pair adjacent to the center should be close doublets. His theory assumes that the electrons in such a diatomic molecule as that of HCl have a resultant angular momentum parallel to the nuclear angular momentum and directed either in the same or in the opposite sense. The magnitude of the electronic angular momentum is assumed to be such that the total angular momentum of the molecule is always an integral number of Bohr units. In this particular case (HCl) the electronic angular momentum is thought to be a half unit. The doublet structure of the band lines is a consequence of assigning slightly different energies to molecules having the same nuclear angular momentum but reversed directions for the electronic angular momentum. Ruling out all states for which the total angular momentum is zero then accounts for the absence of the "null" line at the center of the band and at the same time predicts that one component of each of the adjacent lines will be absent.

If this theory were correct, the intensities of the innermost lines of the two branches would not fit into a continuous series with the intensities of the other lines, but would be half as great as an extrapolation from the rest of the series would suggest. As a matter of fact the intensities of the lines in question show no such anomaly and we may conclude that their structure is the same as that of the other lines in the band.

The difficulty is not a serious one, however, for according to a modification of Kratzer's theory worked out by Kramers and Pauli the electronic angular momentum should always have the same sense as the nuclear angular momentum and the band lines should all be single. Some of the bands in the visible and ultra-violet region are made up of doublets which seem to bear out Kratzer's point of view while others are made up of single lines which fit better with the theory of Kramers and Pauli. The conclusion to be drawn from the intensities of the inner lines of the HCl band at 3.5μ is then simply that it belongs to the latter class.

Supplementary Note: Proof of Formulas (11)

The determination of the amplitudes in the formal Fourier development (9) involves the solution of the dynamical problem of the motion of the two atoms which make up the molecule. Let m_1 and m_2 denote the masses of the atoms, let ρ be the distance between the nuclei, and let $\varphi(\rho)$ be the net force of attraction. Then, as is well known, the dynamical problem reduces to that of a single particle of mass μ given by the formula $\mu = m_1 m_2/(m_1+m_2)$ revolving about a fixed center of force under the influence of an attractive force $\varphi(\rho)$.

It is convenient to use the equations of motion of the particle referred to the rotating set of axes x', y' of Eq. (9). These are

$$\mu \frac{d^2x'}{dt^2} = -\frac{x'}{\rho}\phi(\rho) + \mu\omega_r^2 x' + 2\mu\omega_r \frac{dy'}{dt};$$

$$\mu \frac{d^2y'}{dt^2} = -\frac{y'}{\rho}\varphi(\rho) + \mu\omega_r^2 y' - 2\mu\omega_r \frac{dx'}{dt}.$$

The elimination of $\varphi(\rho)$ yields

$$x'\frac{d^2y'}{dt^2} - y'\frac{d^2x'}{dt^2} = -2\omega_r\left[x'\frac{dx'}{dt} + y'\frac{dy'}{dt}\right]. \qquad \text{(a)}$$

This equation is immediately integrable, but it is convenient to use it as it stands, substituting for x' and y' their Fourier expansions and equating the coefficients of corresponding terms separately to each other.

We assume that x' and y' are proportional to M_x' and M_y'. Without loss of generality we may suppose that the x' axis coincides with the major axis of the orbit so that δ is equal to zero. The following equations are then easily derived from (9)

$$x' = \Sigma\, a_\tau \cos 2\pi\tau\omega_v t, \ (\tau = 0 \text{ to } \infty) \qquad \text{(b)}$$
$$y' = \Sigma\, b_\tau \sin 2\pi\tau\omega_v t, \ (\tau = 0 \text{ to } \infty)$$

where

$$a_\tau + b_\tau = aR_\tau; \quad a_\tau - b_\tau = aR_\tau'; \qquad \text{(c)}$$

and a is a constant. For the present approximate investigation we may break off the series (b) after the terms for which $\tau = 2$. Furthermore, as the motion is only slightly elliptical, we may simplify Eq. (a) by neglecting $y'\ dy'/dt$ in comparison with $x'\ dx'/dt$. The substitution of the initial terms of (b) into (a) then yields

$$b_1 = -\ 2\frac{\omega_r}{\omega_v} a_1 \left[1 - \frac{a_2}{a_0} - \frac{3}{16}\ \frac{a_1^2}{a_0^2}\right], \tag{d}$$

$$b_2 = -\ \frac{\omega_r}{\omega_v} a_2 \left[1 + \frac{a_1^2}{4a_0 a_2}\right]. \tag{e}$$

The vibrational motion of a molecule having not more than one quantum of vibrational energy should be approximately simple harmonic so that a_2 should be small compared with a_1. As the vibrational amplitude is small compared with the mean distance between the nuclei a_0, it follows that the factor in brackets in Eq. (d) is not very different from unity. Combining (d) with (c), we then obtain

$$R_1 = \frac{a_1}{a}\left[1 - 2\frac{\omega_r}{\omega_v}\right]; \qquad R_1' = \frac{a_1}{a}\left[1 + \frac{2\omega_r}{\omega_v}\right].$$

Treating ω_r/ω_v as a small quantity, a further approximation yields

$$R_1 = \frac{a_1}{a}\left[\frac{\omega_v}{\omega_v + \omega_r}\right]^2; \qquad R_1' = \frac{a_1}{a}\left[\frac{\omega_v}{\omega_v - \omega_r}\right]^2. \tag{f}$$

These equations reduce to the form (11) when A is introduced as an abbreviation for a_1/a.

It remains to show that the variation in the product $A\,\omega_v^2$ or $a_1\omega_v^2$ may be neglected in comparison with that of $(\omega_v \pm \omega_r)^2$. The application to be considered has to do with the relative values of R_1 and R_1' worked out for a series of motions corresponding to the different lines in the fundamental rotation-vibration band. The vibrational quantum number for all these orbits is the same, viz., $n = \bar{n} = 1/2$, while the rotational quantum number is equal to the ordinal number $(\bar{m})$ of the corresponding band line. The vibrational energy for a constant vibrational quantum number should be roughly proportional to the frequency of vibration as in the Planck linear oscillator. Hence the variation of the frequency ω_v with $\bar{m}$ is accompanied by a variation in the vibrational amplitude a_1 of such a character that to a first order approximation

$$a_1^2/\omega_v = \text{Const.},$$

or

$$a_1\omega_v \ \sim \omega_v^{5/2}. \tag{g}$$

In order to estimate the relative variation of the factors $\omega_v^{5/2}$ and $(\omega_v \pm \omega_r)^2$ with $\bar{m}$ we make use of the theorem that the frequency of any spectrum line is equal to a suitable mean value of the corresponding classical frequency taken over a series of hypothetical orbits intermediate between the initial and final states. It follows from this theorem that the frequency of any line in the positive branch is

$$\nu^+(\bar{m}) = \bar{\omega}_v + \bar{\omega}_r, \tag{h}$$

while the frequency of a line in the negative branch is

$$\nu^-(\bar{m}) = \bar{\omega}_v - \bar{\omega}_r. \tag{i}$$

The mean frequencies $\bar{\omega}_v$ and $\bar{\omega}_r$ are nearly equal to the values of ω_v and ω_r for the intermediate orbit whose quantum numbers are $\bar{n}$ and $\bar{m}$. Hence we may eliminate $\bar{\omega}_r$ between (h) and (i) by using the frequencies of corresponding lines in the two branches. Thus

$$\omega_v(\bar{m}) = \tfrac{1}{2}[\nu^+(\bar{m}) + \nu^-(\bar{m})]. \tag{j}$$

The above formula permits the evaluation of ω_v from the spectroscopic frequencies of the band lines. In the case of the HCl band at 3.5μ, ω_v (1), the vibrational frequency associated with the central components of the band, is 1.4 per cent greater than ω_v (12) and $[\omega_v (1)]^{5/2}$ is 3.5 per cent greater than $[\omega_v (12)]^{5/2}$. On the other hand the value of $(\omega_v \pm \omega_r)^2$ for the 12th line of the positive branch (i.e. the square of the frequency of that line) is 41 per cent greater than the corresponding value for the 12th line of the negative branch. For this reason it seems permissible to treat $\omega_v^{5/2}$ and $a_1\omega_v^2$ as constant across the band in the present approximate calculations.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
October 11, 1924.

ON THE MERCURY LINE 2270A (1S−2p₁)

By T. Takamine and M. Fukuda

Abstract

Excitation of the mercury line λ2270.—In a previous experiment by Hansen, Takamine and Werner, the line λ2270 ($1S-2p_1$) was found to be excited either in a condensed discharge or in a strong magnetic field. By using the method employed by Metcalfe and Venkatesachar for the study of the absorption of mercury lines, it was found that the glow in the branched arc of a special kind of mercury lamp emits this line with considerable intensity. Under best circumstances, its intensity was stronger than the arc line 2302 ($2p_3-9d_3$), but fainter than 2323 ($2p_2-8d_2$).

Shift of the mercury arc lines 2270, 2345 and 2564 in a condensed vacuum tube discharge.—When analyzed by a large Hilger quartz spectograph of the Littrow type, it was found that in a heavy condensed discharge the lines 2270 ($1S-2p_1$) and 2345 ($2p_3-5s$) are shifted about 0.1A towards the red, whereas the line 2564 ($2p_2-4S$) is displaced about 0.1A towards shorter wave-lengths relative to their positions in an ordinary arc spectrum.

PART I. THE LINE 2270

IT is a remarkable fact that, of the three transitions of an electron in a mercury atom, represented by $1S-2p_1$, $1S-2p_2$ and $1S-2p_3$, we see optically only $1S-2p_2$ (2536), while the other two, namely $1S-2p_1$ (2270) and $1S-2p_3$ (2655), have not been observed at all except by the indirect method of measuring the ionization by impacts of electrons on atoms by Franck and Einsporn.[1]

In 1922, at the suggestion of Prof. N. Bohr, one of the authors[2] in conjunction with Prof. H. M. Hansen and Dr. S. Werner tried to find out how to make the transitions from these two meta-stable states $2p_1$ and $2p_3$ to the normal state $1S$ possible. As the result, it was found that neither a homogeneous electric field nor a magnetic field produces the line $1S-2p_1$ or $1S-2p_3$. On the other hand, the line $1S-2p_1$ is excited with considerable intensity by passing a condensed discharge in a Geissler tube whereas the line $1S-2p_3$ has not been detected at all.

In the experiment above cited, it is to be remarked that there is always the possibility that the line 2270 we observed may be one of the numerous spark lines of mercury; nevertheless that chance of coincidence is very

[1] Franck and Einsporn, Zeits. f. Phys. **2**, 18 (1920)

[2] H. M. Hansen, T. Takamine and S. Werner, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. **3**.

small, and moreover, there was an indication that the line 2270 behaves to a certain extent as though independent of the spark lines.

In the present experiment we tried to examine the conditions favorable for the excitation of the line 2270 in more detail, our special effort being made to produce it in a pure mercury arc spectrum.

We have tried by quite a variety of methods to excite the line 2270, either in a spark spectrum, or in an arc spectrum. As the source of light, we used a large number of Geissler tubes of different forms, as well as vacuum arc, arc in air, arc in argon etc.

For taking the spectrograms, we used Hilger quartz spectrographs of the sizes E_1, E_2 and E_3.

In the case of spark spectra, there were always a large number of lines that came out and behaved similarly to the line 2270, making it rather difficult to distinguish the line 2270 from spark lines.

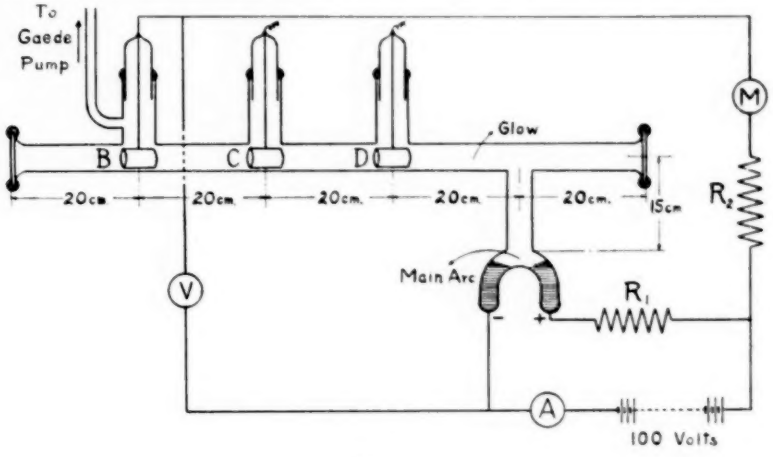

Fig. 1.

Of the many ways tried for getting the line 2270 in an arc spectrum, the method we finally adopted was that found by Metcalfe and Venkatesachar[3] for the study of absorption of mercury lines.

Our experimental arrangement is sketched in Fig. 1. It differs from that employed by Metcalfe and Venkateschar only in that we used a stronger current in the glow of the branched arc.

In Fig. 1, A is the ammeter, V the voltmeter and M the milliammeter; $R_1 R_2$ are the resistances for the main and the branched arcs respectively; B, C, D are the three auxiliarly electrodes, consisting of iron cylinders, to make the branched arc of different lengths. It was the glow of this

[3] Metcalfe and Venkatesachar, Proc. Roy. Soc. A **100**, 149-166 (1921); A **105**, 520-531 (1924).

side arc in the horizontal tube which showed the line 2270 with considerable intensity. Four tubes having the diameters 1, 1.7, 2, and 3 cm were tried with the lengths of 20, 40 and 60 cm. The electrodes of the main arc were cooled by immersing them in water, while all the joints of the upper electrode, as well as the quartz windows at both ends of the tube, which were all cemented on with de Khotinsky cement, were cooled by wet cotton.

To start the glow, the main arc was first lighted and kept at about 2 amperes at 12 volts, then the vertical part of the tube and also the horizontal part near it were heated either by a Bunsen burner or electrically. When long glow was used, it was found necessary to keep the tube hot electrically. The tube was kept continually evacuated by means of a Gaede mercury pump.

The current passing through the glow was varied from 10^{-3} to 2 or 3 amperes, with a terminal voltage of 50 to 90 volts. The spectrum of this glow was very nearly the same as that of the ordinary arc except that it showed the line 2270 and a few bands, especially one at 2345 quite strongly.

With the quartz spectrograph E_1, fairly strong images of the line 2270 could be obtained with an exposure of 10 or 15 minutes. The relative intensity of the line 2270 to that of the ordinary arc lines varied greatly according to the current intensity in the glow. When tubes having different diameters of bore were tried, it was found that there is an optimum current density for a certain diameter of the tube. A very convenient way for getting an estimation of the intensity of 2270 was to compare it with diffuse series lines ($2p_2-md_2$). Starting with a very weak current in the branched arc, we get at first 2270 fainter than a high diffuse term such as $2p_2-12d_2$ or $2p_2-11d_2$. Then by decreasing R_2 we could strengthen the line 2270 gradually so that its intensity came to fall between $m=8$ and $m=9$. But above this point increase of current density only weakened the relative intensity of 2270.

One of the photographs showing the line 2270 stronger than 2303 ($2p_2-9d_2$,), but fainter than 2323 ($2p_2-8d_2$), is reproduced in Plate IA. It is to be remarked here that close to the line 2303 ($2p_2-9d_2$), comes the line 2302 ($2p_3-6d_3$), which being not quite well resolved on the reproduction, renders the estimation of the intensity rather difficult.

As the question of a new line is always associated with that of the purity of the source, great care was taken to use distilled mercury and to keep the discharge tube as clean as possible. In the case of the condensed discharge which was used in our experiment at Copenhagen, impurity lines due to carbon and silica appeared on many occasions. In the present

experiment, however, the lines were almost entirely those of the Hg arc spectrum. Moreover filling the tube with other gases like argon or bromine did not particularly enhance the line 2270.

As to the line 2655 ($1S-2p_3$), we failed to see any trace of it in the spectrum due to the glow of the branched arc.

PART II. CHANGE OF WAVE-LENGTH FOR CERTAIN MERCURY LINES IN A CONDENSED DISCHARGE

While studying the conditions for exciting the line 2270 strongly, we noticed that the line 2270 as produced by a condensed discharge has a slightly longer wave-length than when produced in the side glow of an arc. The amount of this small shift was about 0.1 A.

As the condensed source of light we used an ordinary Geissler tube of the end-on form, having a quartz window at one end. The tube was made of Jena glass and was provided with tungsten electrodes. The capillary part had the diameter of 8 mm and was 6 cm long. For excitation, two 0.4 kw transformers connected in parallel were used, with 220 volt, 3 phase alternating current in the primary. The primary current was usually 9 or 10 amperes. In the secondary circuit, a capacity of four small (200 cc) and two large (400 cc) Leyden jars were put in parallel with the discharge tube. With this arrangement, the capillary portion of the tube appeared faint violet in colour, showing the red mercury line 6149 quite strongly. As the source was very bright, an exposure of several minutes was quite sufficient for most cases.

In order to determine the small differences in wave-lengths of these particular lines, a screen having a suitable shape was made to slide over the slit of the spectrograph, enabling the spectrum of a condensed discharge to be taken in the middle, and that of an ordinary arc, or of a glow in the side-arc, on each side. To obtain the ordinary arc spectrum of mercury, we used an Arons mercury lamp provided with a quartz window. All the lines coming from this source showed perfect coincidence with those due to the glow of the branched arc described in Part I, thus showing that the small shift in the wave-length of certain lines is to be taken as characteristic of a condensed discharge.

As the amount of difference in wave-length under discussion is very small, the question naturally arises if this is not due to the method of projection of the image of the source of light on the slit of the spectrograph; however, this is clearly shown not to be the case when we examine the lines such as 2378, 2302, which are very narrow and sharp, showing perfect coincidence of wave-length on the same spectrogram.

The line 2270, as excited by a condensed discharge, shows a very faint companion on the red side of the main line, at a distance of about 0.2 A.

The amount of shift differed slightly on different plates. The mean of measurements on four different plates is given in Table I.

TABLE I

Shift of wave-length in condensed discharge

Wave-length	Series	Shift
2270A	$1S-2p_1$	+0.1A
2345	$2p_3-5s$	+0.1
2464	$2p_3-4s$	+0.3
2564	$2p_2-4S$	−0.1

Looked at from the series relation, it seems worthy of note that $2p_3-4s$ and $2p_3-5s$ show shifts in the same direction, namely toward the red, while $2p_2-4S$ is displaced to the violet. Further, on a few plates there is an indication that the line 2441 ($2p_2-5S$) is also displaced to the violet. From these data, we may safely conclude that the discrepancies of wave-length in the lines of the mercury arc spectrum, when produced by a condensed discharge as compared with an ordinary arc, seem to have a certain definite connection with the series relations.

In the case of the line 2464, we see a single strong line in the glow spectrum, whereas in the spectrum due to a condensed discharge, a faint line is seen in the original position and a much stronger line on its red side at a distance of about 0.3 A.

Photographs showing the shift of the lines 2270, 2345 and 2464 are reproduced in Plate I (B, C and D). The short middle part is due to the condensed discharge, while the upper and lower parts are due either to the ordinary arc, or to the glow in the branched arc.

A trial was made to see if the amount of shift varied as we changed the mode of excitation from a slightly condensed discharge to a very heavy one by increasing the capacity; but so far, we did not get any definite results. Further experiments in the same direction in which the terminal potential of the discharge is changed by increasing the length of the capillary part and also the influence of foreign gases in the tube is determined, will be tried in the near future.

In many cases, we are confronted with the problem whether or not the lines in a pure arc spectrum undergo a change in their structure as we go from arc to spark spectrum. As a typical case, we may take that of the triplet 2482 ($2p_2-5d_i$), where, close to the original triplet in the arc, we see a group of 8 or 9 lines clustering together in the spectrum due to the condensed spark. It would seem that a further study dealing with the manner of transition from the arc to the spark spectrum would be of much interest.

It must be admitted that there is always the possibility that the lines excited by a condensed discharge are not physically related to the corresponding arc lines, or in other words that their proximity in the arc and spark spectra may be entirely accidental. The question remains open so

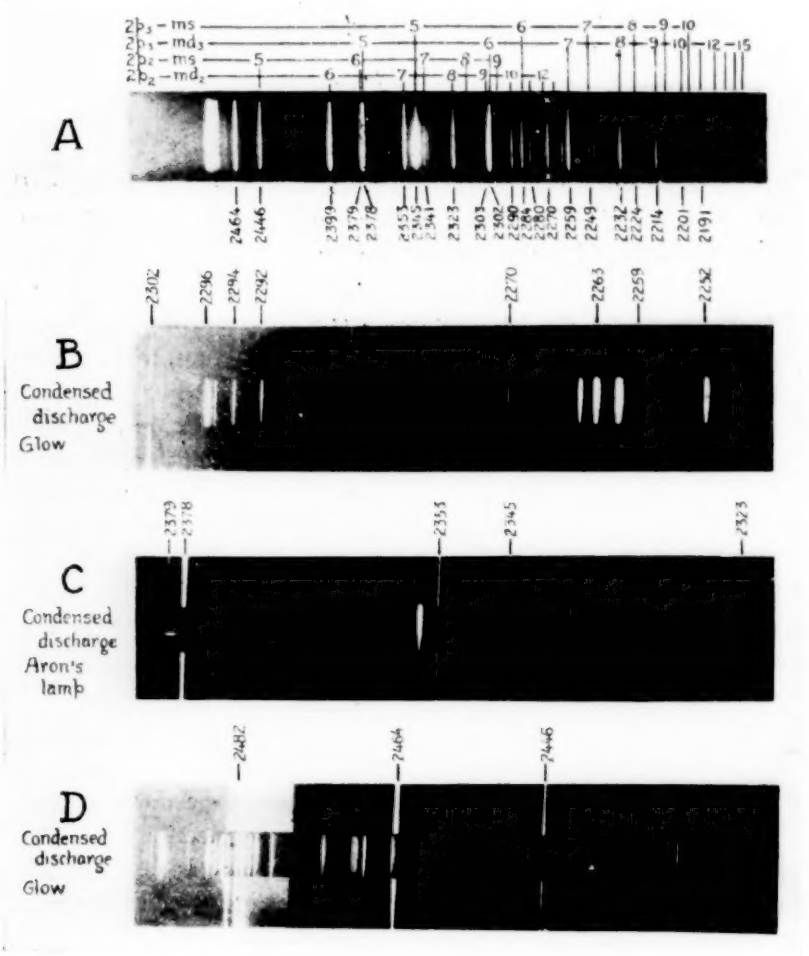

Plate I.

long as we do not have evidence that the lines are physically related, such as might be given by their behavior in an electric or a magnetic field.

As to the cause of this small discrepancy in wave-length of these mercury lines, it seems difficult to draw any definite conclusion at the present stage of our experiment. The interpretation that this may be

due to a Doppler effect seems not to be the right one, for, in the condensed discharge, which was fairly well rectified, we could see no change as to the amount and direction of the shift when the positive and negative electrodes were interchanged.

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ON THE INFLUENCE OF TEMPERATURE UPON THE PHOTO-ELECTRIC EFFECT

By J. Rud Nielsen*

Abstract

Photo-electric threshold frequency for metals.—*Free electron theory.* A discussion is given of the suggestion by Millikan that in the photo-electric effect the energy of the light is transferred to the free electrons of the metals as well as to the bound electrons, and the threshold frequency ν_0 is interpreted by the equation $h\nu_0=\varphi_p-E_k$ where φ_p is the work necessary to remove a free electron from the metal. In cases where E_k is not small compared with φ_p the theory leads to a lack of sharpness in the definition of ν_0. Neglecting variations of kinetic energy, the difference of stopping potentials comes out equal to the Peltier coefficient; hence the uniformity of stopping potentials for different metals observed by Millikan is due, according to the theory, to the smallness of the Peltier effect. *The variation of the long wave-length limit with temperature* comes out $\partial\lambda_0/\partial T=(\lambda_0^2/hc)e\sigma$, σ being the Thomson coefficient. In most cases λ_0 should be practically independent of temperature. *In the case of aluminum,* after prolonged heating, the photo-electric current due to λ2537 was found to remain constant within 1/2 per cent as the target was cooled from 400° to 100°C and this constancy is interpreted as evidence that the shift of the long wave-length limit with change of temperature is less than 1A. The limit was found to be at about 2700A. Similar observations with a nickel target and 2412A gave inconclusive results, as in spite of heating to 1300°C and reduction of the oxide on the surface by heating in hydrogen, reproducible results were not obtained.

Photo-electric current from aluminum for λ2537.—(1) *Effect of prolonged heating* in vacuum by high frequency induction for many hours to near the melting point. The current remained strong. (2) *Effect of cooling from* 400° *to* 100°*C.* The current remained constant within 1/2 per cent.

Introduction

THE influence of temperature upon the photo-electric effect has been studied by a number of investigators,[1] all with negative results. The photo-effect was found independent of temperature within the experimental errors. In the earlier investigations monochromatic light was not used, and the errors of observation were large. Koppius[1] recently determined the long wave-length limit of platinum, and found it independent of temperature to less than 1A for the range 50° to 500°C. Other experi-

* Fellow of the American-Scandinavian Foundation, 1922-23.

[1] Lienhop, Ann. der Phys. **21,** 281 (1906);
Dember, Ann. der Phys. **20,** 379 (1906); **23,** 957 (1907);
Ladenburg, Verh. d. Deutsch. Phys. Ges. **9,** 165 (1907);
Millikan and Winchester, Phil. Mag. **24,** 188 (1907);
Kunz, Phys. Rev. **29,** 174 (1909);
Koppius, Phys. Rev. **18,** 443, (1921).

ments,[2] however, have shown that the apparent long wave-length limit of platinum is gradually decreased as the surface is being denuded of occluded gases by prolonged heating at higher and higher temperatures. The question as to whether or not the photo-electric sensitivity is an intrinsic and invariable property of metals has thus been raised again.

In the present investigation the variation of the long wave-length limit to be expected from a theoretical standpoint is discussed, and an attempt has been made to determine the temperature variation upon surfaces freed from gases as well as possible by heating in vacuum.

1. Interpretation of the Long Wave-Length Limit

In 1921 Millikan[3] found that the "stopping potential," i.e. the potential that must be applied in order to prevent the photo-electrons from reaching the receiver, is quite accurately the same for different emitting metals, provided the same receiver is used. From earlier experiments by Hermann[4] and Page[5] a similar inference may be drawn. This peculiar fact led Millikan to the conclusion that *the electrons which escape from a metal with the maximum velocity under the influence of light are the free, i.e. the conduction electrons of the metal.* On account of the great importance of this result for the interpretation of the photo-electric phenomena a brief discussion of it will be given. It will be shown that it furnishes an interpretation of the long wave-length limit, and leads to definite conclusions as to the temperature variation.

It is immaterial for the analysis here given whether we assume that the light energy is transferred *directly* to the free electrons of the metal or indirectly, as suggested by Epstein, through collisions of the second kind. Millikan's conclusion is that the light energy $h\nu$ is transferred undiminished to electrons which are in the same state as those emitted as thermo-electrons. Very little is known about the conditions of the free electrons. We shall, therefore, make no special assumptions but use only two equations, which were derived by O. W. Richardson[6] from purely thermodynamical though not quite rigorous considerations. These equations are

$$\partial\phi/\partial T = (3/2)k - e\sigma \tag{1}$$

$$\phi' - \phi'' = eV - eT\,\partial V/\partial T \tag{2}$$

[2] Hallwachs, Phys. Zeitschr. **21,** 561 (1920);
Sende and Simon, Ann. der Phys. **65,** 697 (1921);
Suhrmann, Ann. der Phys. **67,** 43 (1922);
Tucker, Phys. Rev. **22,** 574 (1923).

[3] Millikan, Phys. Rev. **18,** 236 (1921)

[4] Hermann, Verh. d. Deutsch. Phys. Ges. **14,** 557, 573, 936 (1912)

[5] Leigh Page, Am. Jour. Sci. **36,** 501 (1913)

[6] Richardson, The Emission of Electricity from Hot Bodies, London 1916, pp. 32, 41.

where ϕ is the increase of energy which accompanies the transference of an electron from the interior of a metal to a point outside, ϕ' and ϕ'' being the values for two different metals. T denotes the absolute temperature, k Boltzmann's constant, e the charge of an electron, σ the coefficient of the Thomson effect, and V the contact difference of potential between the two metals. The term $eT\,\partial V/\partial T$ may also be written eP, P being the Peltier coefficient. The terms $e\sigma$ and $eT\,\partial V/\partial T$ are, in general, small compared with the other terms in the equations. As Bohr[7] has pointed out, P and σ are not identical with the coefficients found by experiment, but this fact is of little importance for the present considerations.

We will denote by E_p the potential energy of a free electron, and by E_k its average kinetic energy within the metal, and will place $\phi=\phi_p+\phi_k$, where ϕ_p is the gain in potential energy and ϕ_k the gain in kinetic energy accompanying the transference of a free electron from the metal to the surrounding electron atmosphere. If the heat energy of the electron atmosphere be assumed equal to that of a monatomic gas, we have $\phi_k=(3/2)kT-E_k$.

We are now prepared to give an interpretation of the term $h\nu_0$ in the expression for the maximum kinetic energy of the photo-electrons, which was predicted by Einstein and verified by Millikan, viz.

$$(V_s+V_F)e=h\nu-h\nu_0, \tag{3}$$

where V_s denotes the stopping potential, and V_F the contact difference of potential between emitter and receiver. If, following Einstein, we assume that the energy $h\nu$ of a light quantum is transformed to kinetic energy of a single electron, and if we disregard the fact that the kinetic energy is not the same for all the free electrons, then the largest possible value of the kinetic energy of a photo-electron escaping from the metal must be approximately $E_k+h\nu-\phi_p$. The frequency ν_0 for which this is zero is the threshold frequency, and we have

$$h\nu_0=\phi_p-E_k. \tag{4}$$

Instead of using this expression for $h\nu_0$ Millikan[3] placed $h\nu_0$ equal to ϕ' a value which is $(3/2)kT$ larger. This, however, did not influence his result for relative values because the value of $h\nu_0$ for one metal was subtracted from that for another.

Substituting for $h\nu_0$ in (3) and subtracting the equations for two different metals we get

$$-(V_s'-V_s'')e+Ve=\phi_p'-\phi_p''-E_k'+E_k'',$$

[7] Bohr, Phil. Mag. **23**, 984 (1912)

where $V = V_F'' - V_F'$ is the contact difference of potential between the two metals. Now substituting the value for Ve obtained from (2), and remembering that $\phi_k + E_k = (3/2)kT$, we simplify the equation to

$$-(V_s' - V_s'') + T\,\partial V/\partial T = 0. \qquad (5)$$

The last term in (5), from the values of the measured Peltier coefficients, is of the order of magnitude of 10^{-3} to 10^{-2} volts. Millikan's conclusion that the light energy is transferred to the free electrons of the metal, leads, therefore, to a simple explanation of his experimental result that the stopping potential does not depend upon the nature of the emitter. From (5), however, it will be seen that *accurate measurements of stopping potentials should reveal slight differences approximately equal to the Peltier coefficients, expressed in volts.* It would be of great importance for the theory if determinations of stopping potentials could be made so accurately as to allow a test of (5).

The expression (4) for $h\nu_0$ is valid only when the differences in the kinetic energies of the free electrons may be disregarded. It will, therefore, not hold at high temperatures. Under such conditions, according to the free electron theory, an appreciable lack of sharpness in the definition of the threshold frequency and of the stopping potential should occur.

It seems impossible to explain the equality of stopping potentials for different metals by any other simple theory of the photo-electric effect. The assumption that the light energy is transferred to electrons bound in the atoms would imply, as shown by reasoning similar to that given above, that the electrons bound in atoms of different metals possess the same energy. This is at variance with all we know about atomic structure. The assumption that the uniformity of stopping potentials is due to a uniform gas layer on all metals would lead also to a uniform threshold wave-length and to a uniform photo-electric sensitiveness, due corrections being made for differences in reflecting power, but this does not seem to be in accord with observations.

The hypothesis that a quantum of light energy can be transferred entirely to a free electron may seem rather strange. It may, therefore, be worth while to note that it may be reached by a natural generalization of the ideas by which the continuous absorption spectrum of hydrogen or sodium is explained. It is assumed that when light of a shorter wave-length than the limit of the absorption series is absorbed, the electron is knocked out with a kinetic energy equal to the difference between $h\nu$ and the work necessary for ionization. But if this absorption process may take place however loosely the electron be bound, it should also occur in the limiting case of the free electron.

2. Temperature Variation of the Long Wave-length limit

The influence of a change in temperature upon the threshold frequency ν_o may be found immediately from the theory discussed above, since $\phi = \phi_p + (3/2)kT - E_k$, Eq. (1) may be written $\partial(\phi_p - E_k)/\partial T = -e\sigma$; but $\phi_p - E_k = h\nu_o$, hence

$$\partial(h\nu_o)/\partial T = -e\sigma \tag{6}$$

or

$$\partial\lambda_o/\partial T = (\lambda_o^2/hc)\, e\sigma, \tag{6a}$$

$\lambda_o = c/\nu_o$ being the long wave-length limit.

The temperature variation of the threshold frequency or of the long wave-length limit is thus proportional to the Thomson coefficient. Since the Thomson effect is always very small, the long wave-length limit should be practically independent of temperature. For aluminum Borelius and Gunneson[8] have found $\sigma = -0.56$ microvolts per degree at 400°K, while $\lambda_o = 2700$ A. Substituting these values we get $\partial\lambda_o/\partial T = 3.3 \times 10^{-4}$ A per degree, i.e. a shift in long wave-length limit of 1/10 A for a change in temperature of 300 degrees. For all the metals for which both σ and λ_o are measured, (6a) gives so small values for the temperature variation that, with the accuracy with which photo-electric measurements are now being carried out, it should not be possible to detect the variation. For the alkali metals, however, a measurable variation may be expected since σ is large, as indicated by the values found for the specific heats, and since λ_o is also large.

In the preceding only the long wave-length limit has been considered. No satisfactory theory has yet been given for the velocity distribution nor for the magnitude of the photo-electric saturation current. The reason for this is partly the lack of a satisfactory substitute for the old electron theory of metals and partly the lack of reliable photo-electric data. We shall, therefore, not attempt to treat theoretically the effect of temperature upon the photo-electric current.

3. Experimental Method and Apparatus

A variation in the long wave-length limit has been searched for by observing the photo-electric saturation current at different temperatures of the emitting metal, using a wave-length just below the long wave-length limit. Actual measurement of a change would require observations with different wave-lengths. If photo-currents are found to be constant, it may be reasonably inferred that the long wave-length limit is independent of temperature.

[8] Borelius and Gunneson, Ann. der Phys. **65**, 520 (1921)

Photo-electric targets of aluminum and nickel were heated in vacuum by high frequency induction. Two Western Electric 212-A tubes, in parallel, served as generators of the high frequency currents which were sent through the primary coil of thick copper tubing surrounding the photo-electric tube. The targets were solid cylinders of diameter 1.9 cm and length 2.0 or 1.2 cm. During the slow cooling of the target the saturation current was measured by the aid of a quadrant electrometer connected to the cylindrical receiver which partly enclosed the target.

Fig. 1 shows the two types of photo-electric tubes used. Both were made of Pyrex glass. A quartz window was cemented on with a high temperature cement. The temperature of the seal was kept below 100°C by water cooling. In tube A, with which most of the experiments with

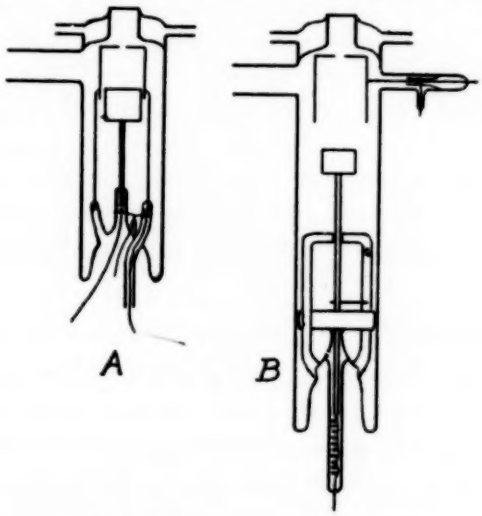

Fig. 1. Photo-electric tubes used.

aluminum were made, the target was fixed with respect to the receiver. When the target was heated the receiver would also be heated. In order to prevent the receiver, which was made of copper, from melting, the heating of the target had to be applied intermittently, so as to let the thin copper cylinder cool for a short time between consecutive heatings. In tube B, which was used for nickel, the target was heated outside the receiver, which was also made of nickel, and then lifted up into the receiver by a simple magnetic device. The light reached the target through a slit in the top of the receiver. To begin with, both tubes had thermo-couples for measuring the temperature of the target. These, however, soon got out of order. In one case the junction moved out of the target at the first heating to the melting point; in another case a discharge took place

from the coil outside the tube to the thermo-couple wire inside. Enough data were obtained, however, to permit an estimate of the temperature during the cooling. The only temperature used for the calibration of the thermo-couples was the melting point of aluminum.

The tubes could not be used very long or the glass would be heated to the softening point by radiation from the target and by currents in the layer of metal deposited on the glass wall by evaporation of the target.

A 220 volts quartz mercury lamp and a Hilger monochromatic illuminator were used for illumination. The lamp was enclosed in an asbestos box and run at a constant high voltage, the voltage drop in the arc alone being about 120 volts. By means of a large quartz lens an image of the arc, of nearly natural size, was formed on one slit of the illuminator and adjusted so that the middle covered the slit. The light then just filled the collimator lens. Under these circumstances the variations in the intensity of illumination were found to be practically negligible. The photo-electric tube was set up vertically so that the quartz window was only a few millimeters from the other slit of the illuminator, the slit in the receiver being large enough to let the slightly divergent light pass to the target. The pressure in the tube was in most cases so low that no reading could be obtained by a McLeod gauge even when the target was heated.

4. The Cleaning-Up of the Aluminum Surface by Heating

With aluminum the photo-currents were so large that they could be measured by the constant deflection obtained when the two pairs of quadrants were shunted with a high resistance consisting of a line of ink on a strip of paper. The sensitiveness of the electrometer was about 1500 mm per volt at a scale distance of 1m. In almost all the experiments with aluminum the line 2537 A was used.

Heating of the target was found to have a great effect upon the photo-electric current. When the aluminum had been exposed to air, or when it had been kept for a long time in a vacuum without being heated, the photo-current was small. A short heating, however, produced a considerable increase in the current; and as the heating was continued and the temperature raised, the photo-current reached a maximum, decreased and then increased again until a value of 5 or 10 times the original was reached. Further heating to a temperature close enough to the melting point produced a decrease in the current. When the aluminum had been heated for a long time, and the melting point had been reached several times during the intermittent heating, the photo-current had attained a value of about one third of the highest value observed, and continued heating

produced no further change of the photo-current. In one case the following values of the current for 2537 A were obtained during the process of cleaning up, the target being heated several times between consecutive values:

6.4, 25.8, 24.0, 18.9, 20.8, 27.7, 43.0, 45.5, 18.5, 17.5.

The effect of the cleaning-up by heating upon the photo-current from aluminum is of the same general character as that found for platinum by other observers.[2] The fact that the photo-current remained strong after prolonged heating at the melting point is an evidence against a fundamental dependence of the photo-effect upon surface impurities, although, of course, the heating had not produced a complete cleaning-up of the aluminum surface. Aluminum oxide, for example, cannot be removed by heating. Close to the melting point, a breaking-up of the surface occurs, so that it becomes granular. Whether the currents are due mostly to aluminum or to the oxide is unknown.

The following observations may be of interest in connection with the problem of the nature of the surface impurities. When the photo-current was observed for a sufficiently long time after the heating, an increase in the current was always observed. However, if the liquid air were removed from a charcoal tube between the photo-electric tube and the pumps, leaving liquid air only on a trap closer to the pumps, a considerable decrease in the current would immediately set in, amounting to about 30 per cent of the original value in two minutes and to 40 per cent in ten minutes.

5. Temperature Variation with Aluminum

As long as the aluminum was not sufficiently cleaned up by heating, a considerable variation of the photo-electric current was observed during the cooling. In all cases the photo-current was found to decrease at first. The current would then generally become almost constant; in some cases, however, an increase followed the decrease. A typical example is given in Fig. 2 Curve 1, the photo-current being plotted against time of cooling. The first readings were taken 2 or 3 minutes after the thermionic current had become negligible, the temperature then being about 400°C. By the time the photo-current had become constant the temperature was about 150°C. The constancy of the current during the last part of the cooling is remarkable. This may be better seen from Table I (A and B) which gives all the readings taken during twenty minutes. The smallness of the variations gives an idea both of the constancy of the light intensity and of the accuracy with which the photo-currents could be measured.

That the decrease observed in the beginning is not due simply to a dependence of the photo-current upon temperature is most clearly brought out by comparing Curve 1 with Curve 2, which was taken immediately after Curve 1, the target having been heated for three minutes to about 400°C between the two sets of readings.

The longer the aluminum was heated and the higher the temperature to which it was heated, the smaller was the variation of the photo-current observed during the cooling. Curve 3 was obtained after the target had been kept red hot for 1½ hours, the temperature never quite reaching the melting point. The total variation of the current is only about 3 per cent. However, in this case the aluminum was not yet cleaned up as much as possible.

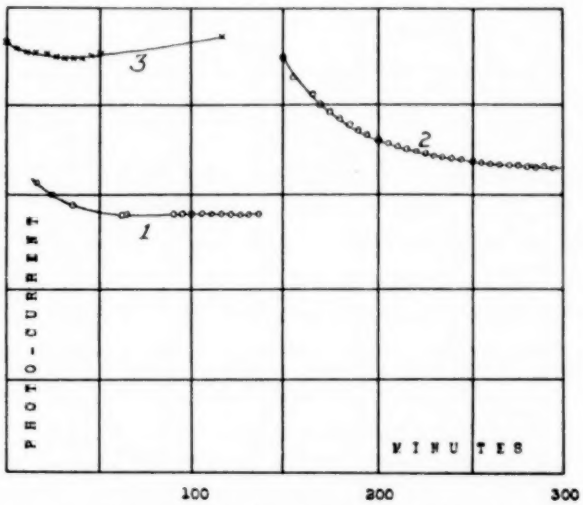

Fig. 2. Photo-currents from aluminum during cooling.

Table I (C) gives the result of the last experiment made with aluminum. The target had now been heated several hours daily for two months. It was very much deformed and displaced, and the next heating resulted in a break-down of the tube. Immediately before the readings were taken the target was heated for one hour, the temperature being kept close to the melting point, which it reached several times. The electrometer zero was determined two minutes before and two minutes after each reading, and corrections were made for a slow motion of the zero amounting to 1.4 cm per hour. Almost no variation of the photo-current is observed during the first 50 minutes of the cooling. The increase at lower temperatures indicates that some surface film is being formed.

The experiments with aluminum have thus failed to detect any variation of photo-currents with temperature between 400°C and room temperature. *In the temperature range 400°C to 100°C the photo-current obtained with 2537 A is found constant within ½ per cent.*

TABLE I

Photo-current from aluminum for 2537A

(A)		(B)		(C)	
Time	Photo-current	Time	Photo-current	Time	Photo-current
110 min.	28.20 cm	120 min.	28.13 cm	0 min.	17.2 cm
111	28.18	121	28.12	10	17.3
112	28.15	122	28.15	20	17.35
113	28.14	123	28.10	30	17.29
114	28.11	124	28.13	40	17.30
115	28.13	125	28.15	50	17.33
116	28.12	126	28.10	62	17.6
117	28.15	127	28.20	70	17.8
118	28.15	128	28.12	80	18.0
119	28.14	129	28.14		

From the constancy of the saturation current we may infer that the temperature variation of the threshold wave-length of aluminum is very small. An estimate of the change in long wave-length limit corresponding to a change in the current for 2537 A of ½ per cent may be obtained in the following way. The curve representing photo-current per unit intensity of illumination as a function of the wave-length will be nearly a straight line in the neighborhood of the long wave-length limit. If we assume that a small change in the limit simply produces a displacement of the curve parallel to the wave-length axis, then a constancy of the current within ½ per cent means a shift of the limit of less than 1 A, the limit being about 150 A from the wave-length used. No accurate determination of the long wave-length limit was made. A rough determination gave for aluminum cleaned up by heating the limit 2700 A, which is much lower than that found by Richardson and Compton.[9]

5. EXPERIMENTS WITH NICKEL

With nickel the results were not nearly as conclusive as with aluminum. The photo-currents were so small that the steady deflection method could not be used. The currents were measured by the rate of charging up of the receiver connected with one pair of quadrants. In order to clean up the target it was heated to 1300-1400°C. The tube could not stand a heating to this temperature for a very long time. Oxide on the surface was reduced by heating in hydrogen. The readings of the photo-current

[9] See Hallwachs' article in Handbuch d. Radiologie, Vol. III.

were started, as with aluminum, as soon as the thermionic current was negligible, which occurred at about 550°C.

A constant current was never obtained. Fig. 3 shows two of the curves obtained with 2412 A. Before Curve I was taken the target had been heated for 15 minutes at 1300-1400°C. Curve II was obtained right after Curve I, the target having been heated for 40 minutes between the two sets of readings. Though the current varies considerably during the

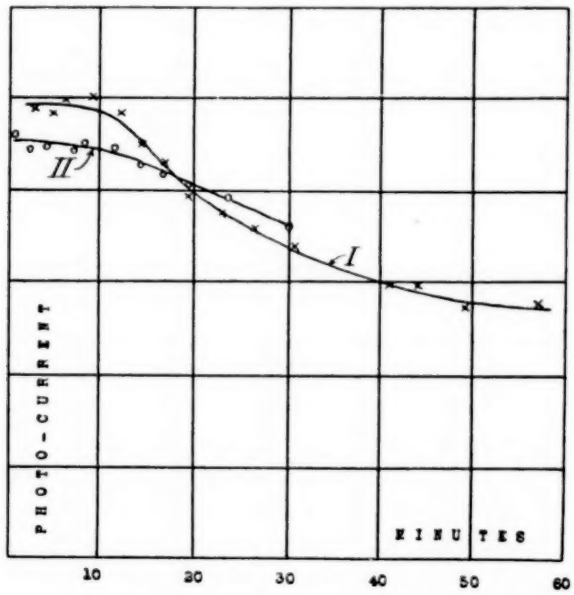

Fig. 3. Photo-currents from nickel during cooling.

cooling, the fact that there is no large variation during the first very rapid cooling indicates that the variation is not due simply to a dependence upon temperature of the photo-electric effect.

The long wave-length limit of nickel was roughly determined at 2500 A.

In conclusion, the writer wishes to express his great indebtedness to Professor R. A. Millikan who suggested the problem and under whose direction the work was done.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
December, 1923.[10]

[10] Received May 16, 1924—Ed.

ELECTRONIC BOMBARDMENT OF METAL SURFACES

By H. E. Farnsworth

Abstract

Secondary electrons from Cu, Ag, Au, W, Pt, Pd, Mg, and Al, produced by electronic bombardment, 0 to 250 volts.—The apparatus used to study the first six metals has been described in a previous paper.[1] The last two metals and especially copper were studied with a modified apparatus constructed out of molybdenum so as to eliminate magnetic effects and permit the study of surfaces condensed from the vapor. (1) Curves are given showing the *ratio of secondary (emergent) to primary (incident) electron current* as a function of the primary velocity. These curves depend on the previous heat treatment of the metals, but after heating the higher melting point metals red-hot for some time, limiting curves were obtained which are characteristic of the different metals. Each curve (except for Cu) rises sharply from the origin but flattens out at a primary velocity of from 3 to 11 volts then rises more slowly showing perhaps a second tendency to flatten. Au and Ag also show a slight kink at 3 volts. The curve for Cu has two sharp maxima at 3 and 6.5 volts, respectively, with two other less distinct ones at about 14 and 20 volts. The secondary electron currents from Mg and Al were extraordinarily large in comparison with those of the other metals, the ratio to primary current for Al reaching a value of 1.8 at 140 volts. (2) *Velocity distribution curves* of the secondary electrons show that, in general, for low primary velocities, most of the secondary electrons have velocities nearly equal to the primary velocity. For higher primary velocities the percentage of secondary electrons having low velocities increases with the primary velocity. The primary velocity for which low velocity electrons begin to leave the surface varies somewhat with the metal but lies between 9 and 15 volts for the metals tested. Curves obtained with a special apparatus consisting of a conducting sphere at whose center the target was placed, show slight kinks indicating *inelastic collisions in copper* at 3 and 6.5 volts velocity, in agreement with the above maxima, but these results are somewhat doubtful. (3) *Variation with the previous treatment of the copper surface.* The results of various experiments show (a) that the removal of gas from the metal decreases the secondary current but does not change the form of the secondary electron curve, and (b) that the characteristic secondary electron curve with various maxima was obtained only from a crystalline surface after any amorphous layer present had been removed, and, within limits, was little affected by exposure to air. The effect of adding an evaporated film of copper was to decrease the secondary current very considerably and to cause the characteristic maxima to disappear. (4) *Effect of simultaneous exposure to radiation from a quartz mercury arc* was merely to add the photo-electric effect to that due to the bombardment.

Effect on the surface of copper of heating in vacuum.—The results indicate that the layer deposited by evaporation is amorphous and that between certain limits of temperature surface crystals of copper are formed.

I. Results with Previously Used Apparatus

THE present experiments are a continuation of a previous investigation[1] which was concerned with: (1) the magnitude of the secondary electron current from nickel as a function of the primary velocity, and (2) the velocity distribution of the secondary electrons for any given primary velocity. The results showed that the secondary electron curve depends very markedly on the previous heat treatment of the metal, but a limiting curve was obtained which did not change with further heating and was also independent of the gas (air and hydrogen) to which the metal had previously been exposed. For this reason this curve was taken to be the true curve for nickel freed from gas as much as possible. The conclusions drawn from these results were (1) that below about 9 volts primary energy, the secondary electrons consist of scattered or reflected primary electrons, (2) that above 9 volts, actual emission of electrons from nickel takes place, the number of emitted electrons increasing with the primary velocity, there being also reflected electrons present whose number decreases with increase of primary velocity.

The present experiments are concerned, first, with obtaining the secondary electron characteristics of other metals, using the same apparatus but changing the targets; and, second, with experiments made with the apparatus modified so as to permit a more detailed and varied study of conditions in certain cases.

For the first part, the apparatus previously used was evacuated and heated in an electric furnace to 400° C for several hours with the pumps working continuously. Liquid air was kept on the condensing trap continually during the time that the tube was connected to the vacuum line. The pumps (oil fore-pump and a mercury vapor pump) were kept going during the observations so that the pressure was less than 10^{-7} mm Hg. Fig. 1 shows the secondary electron curves,[2] i.e., ratio of the secondary to the primary current as a function of the primary velocity, for the metals indicated. These curves were obtained after heating the targets of the various metals at red heat, and represent the limiting curves obtained after heating at this temperature.[3] The curves obtained after

[1] H. E. Farnsworth, Phys. Rev. **20**, 358 (1922)

[2] In the following discussion the term "secondary electron curve" will be used to denote curves of the type shown in Fig. 1 in contrast to "velocity distribution curves" as shown in Fig. 7.

[3] A magnetic field was used to focus the primary electrons during these observations. As was found later, the ratio of the secondary to the primary current when using the magnetic field was smaller than when no field was present. For instance when using no field, the value of the ratio for copper at 250 volts primary velocity was later found to be 1.14 instead of 1.04.

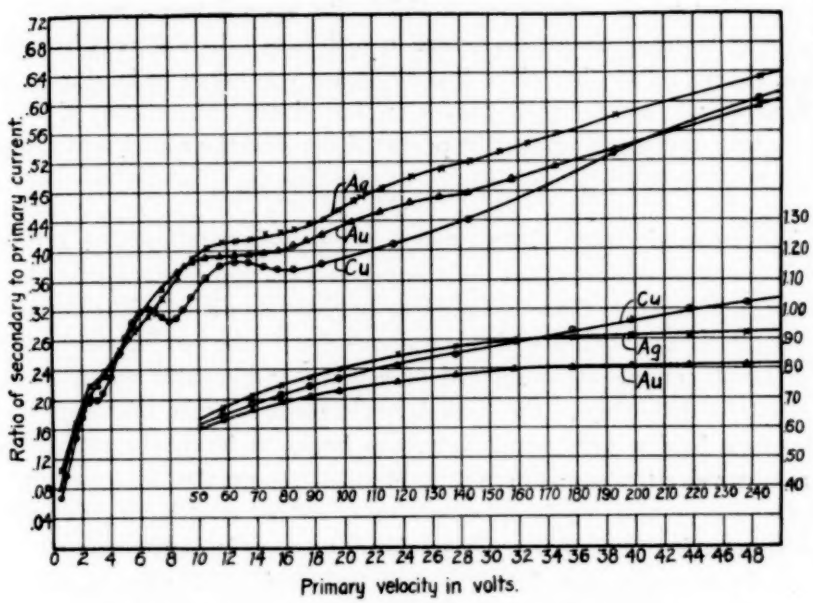

Fig. 1, a. Secondary electron curves for Cu, Ag, and Au after red-heat treatment.

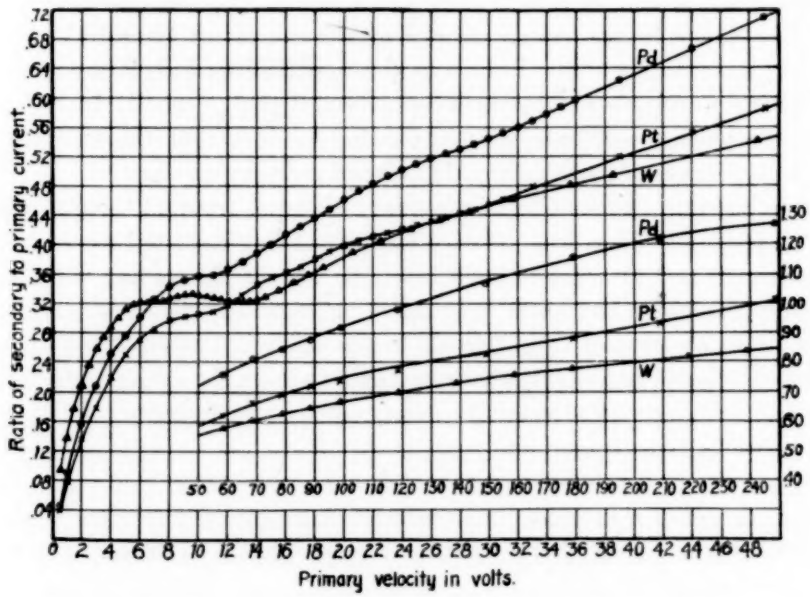

Fig. 1, b. Secondary electron curves for W, Pt, and Pd after red-heat treatment.

baking the whole apparatus at 400°C for several hours but without heating the target at red heat were in each case quite different from the final curves shown, but since this difference was taken to be due to the effect of occluded gas these curves are not given. The curves of Fig. 1 have been corrected for contact potential between the source and target.

II. Discussion of the Results

The curves for the different metals show distinct differences in form. It is therefore obvious that their interpretation will in some cases have to be more complex than that previously given for nickel. The curve for tungsten is the only one which is quite similar to the one for nickel, with the break coming at 14 instead of 9 volts, and measurements of the velocity distribution of the secondary electrons indicate that secondary electrons having very small velocities begin to leave the surface for primary velocities somewhere near 14 volts, the number increasing with the primary velocity, there being also a few per cent having velocities nearly equal to that of the primary beam up to at least 100 volts.

In the case of copper, however, no correlation could be found between the form of the velocity distribution curve of secondary electrons and the maxima or minima of the secondary electron curve. As for the curves for silver and gold, the fact that they are nearly identical suggests that the mechanism producing the effect is similar in the two cases. In each case there seem to be two poorly defined maxima at about 11 and 23 volts.

Since, according to the Bohr hypothesis, palladium and platinum have the same electronic arrangement as silver and gold, respectively, except for one valence electron, it is interesting to note that the secondary electron curves of palladium and platinum are very similar.

The velocity distribution of secondary electrons from all these metals is in general similar, low velocity electrons being detected somewhere between 9 and 15 volts in each case, the number increasing with the primary velocity, but since the rate of increase for the lower primary velocities is very slow, it is difficult to determine accurately the voltage at which these low-velocity electrons begin to leave the surface. In each case, a few per cent had velocities nearly equal to the primary velocity up to at least 100 volts.

These results are sufficient to show that the phenomena in question are not as simple as was originally supposed (see references given in previous paper[1]) and that the characteristics vary from metal to metal, as might well be expected.

Although the results reported thus far give the secondary electron characteristics for the lower primary velocities, they do not decide the

question as to whether the phenomenon observed is strictly an atomic one or whether it depends upon the mass structure of the metal. Therefore a modified apparatus was constructed.

III. Modified Apparatus

The modified form of apparatus is shown in Fig. 2. This apparatus consists, as before, of (1) an equipotential, nitrate-coated platinum cathode *S*, heated by radiation from a tungsten spiral filament; (2) a

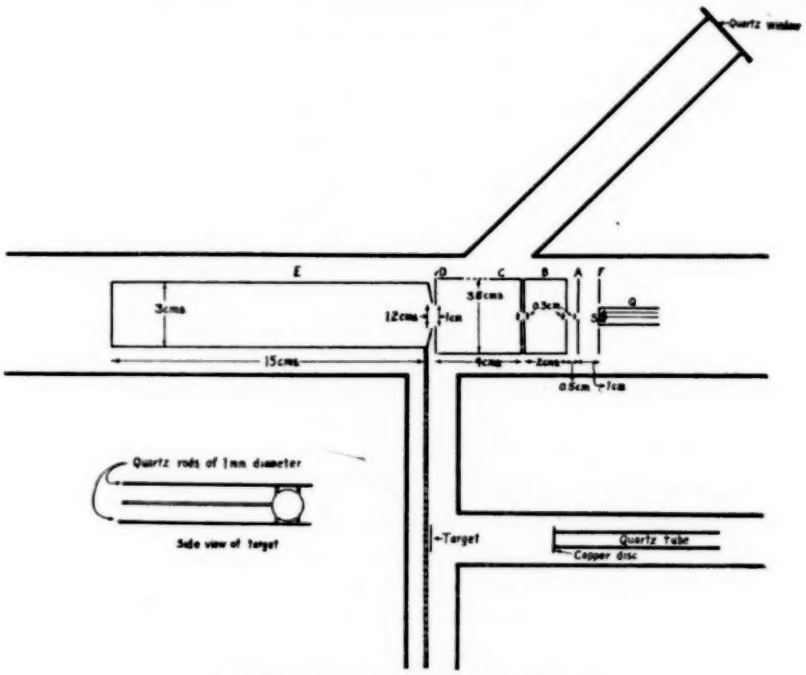

Fig. 2. Modified form of apparatus.

series of insulated diaphragms used to limit the primary electrons and to determine their velocities and those of the secondary electrons; and (3) a Faraday cylinder *E* in front of which the target to be studied can alternately be interposed and withdrawn. The metal parts of this apparatus are constructed of molybdenum instead of nickel, to eliminate any possible magnetic effects. The target can be withdrawn, by means of a magnetic control, into the side-tube where it can be separately outgassed by high-frequency induction and where an evaporated film may be deposited onto it by heating a metal disk in another side-tube. The target and disk are both mounted on quartz so that no other metal becomes hot when these are heated. (The quartz window is platinized

around the edge, then copper plated and soldered to the glass tube with Wood's metal. One end of the main tube is closed by soldering a piece of plate glass over the end of the tube with Wood's metal. This direct seal from Wood's metal to glass proves very satisfactory if proper precautions are taken to clean the glass and metal before soldering.)

The procedure is the same as that used with the former apparatus. With B, C, D, and E at the same potential, the secondary electron current, for any given primary velocity, is determined from the difference between the current to the Faraday cylinder E, and that to the interposed target. The velocity distribution of the secondary electrons is obtained by placing a variable retarding potential on C and D and measuring the secondary electron current as a function of this potential in the usual way.

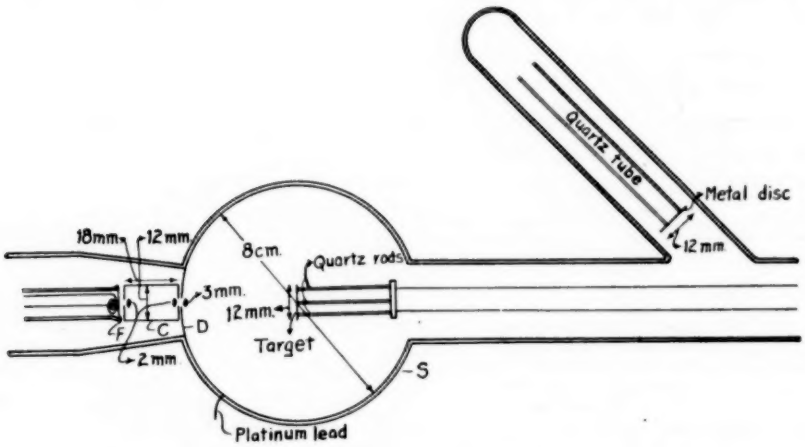

Fig. 3. Apparatus for measuring velocity distribution of secondary electrons.

Before proceeding with the results, a description of another form of apparatus will be given. The apparatus as shown in Fig. 2 is not suitable for an accurate determination of the velocity distribution of the secondary electrons because of the distorted field which exists near the edges of the target when a retarding potential is applied to C and D. To obtain a more accurate knowledge of the velocity distribution, the apparatus shown in Fig. 3 was constructed. The essential feature is the conducting sphere at whose center the target can be placed, thus insuring a uniform radial field when a retarding potential is applied to the sphere. The primary stream of electrons enters the sphere through a 3 mm hole in a platinum diaphragm D sealed into the glass. The inner surface of the glass sphere is made conducting by sputtering with platinum; this also makes contact between it and D. The target may be removed into the

side-tube by means of a magnetic control, where it may be outgassed by high frequency induction and where an evaporated film may be deposited onto it by heating a metal disk in the side-tube inclined at 45°. A diaphragm is automatically raised in the tube between the sphere and target when the target is pulled back, thus preventing any evaporated metal from contaminating the sphere. The target is mounted on three quartz rods which are fastened to a molybdenum framework that slides on glass tracks. It is thus possible to heat the target without heating the framework. The source of electrons is the same as that previously described. The cylinder C is made of molybdenum lined with platinum, with platinum diaphragms on the ends to limit the primary beam. The accelerating potential is applied between the source F and the cylinder C. It is found that the primary beam can be kept from spreading before reaching the target, by maintaining the potential of the cylinder C about 3 volts positive with respect to the sphere. It is also necessary to use large Helmholtz coils to compensate the earth's magnetic field in all of the experiments.

Although this apparatus was originally intended only for observations on velocity distribution of secondary electrons, it is found that results on the ratio of the secondary to the primary current are in good accord with those obtained with the previous apparatus. The current to the sphere is taken as a measure of the secondary current and the total current to the sphere and target as the primary current. This method, of course, neglects multiple reflection between the sphere and target but the fact that the results obtained were so nearly in accord with those from the former apparatus, Fig. 2, is good evidence that any such errors are negligible.

IV. Detailed Study of Copper

After the reconstruction of the apparatus as shown in Fig. 2, several months were spent in a detailed study of copper. This metal was chosen because, of all the metals investigated, the various maxima and minima in its secondary electron curve are more sharply defined than for the other metals, and also because the low melting point of copper enables the surface to be readily evaporated off or a film to be deposited (by heat treatment) from another plate of copper.

The following work on evaporated films was done in an attempt to determine to what extent the characteristics of copper are determined by crystal structure and to what extent by gas content of the metal. Curve 1, Fig. 4, is a typical curve for copper. It is of the same form as that obtained with the former nickel apparatus, except that the maximum

now observed at 20 volts was not then noticeable. This is probably because in the earlier form of apparatus it was not possible to heat the target to such high temperatures as were later used. A curve similar to curve 1 was obtained after the target had been heated for only a few minutes at red heat, but curve 1 was obtained after the target had been heated for about 45 minutes at bright red heat, when the pressure indicated by the McLeod gauge was less than 10^{-6} mm Hg. During this heating the surface of the target had evaporated so that the target appeared very crystalline with a bright copper color. Curve 2 was obtained after copper had been evaporated from a copper disk onto the

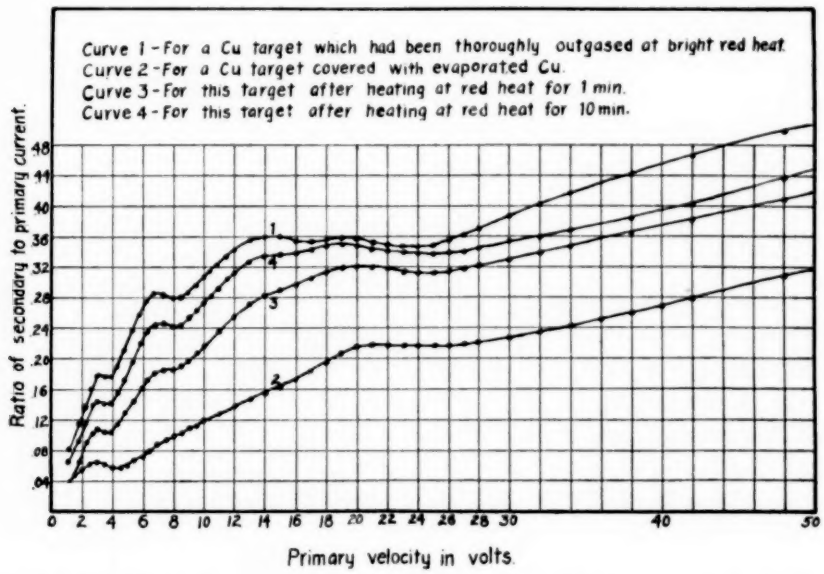
Curve 1 - For a Cu target which had been thoroughly outgased at bright red heat.
Curve 2 - For a Cu target covered with evaporated Cu.
Curve 3 - For this target after heating at red heat for 1 min.
Curve 4 - For this target after heating at red heat for 10 min.
Ratio of secondary to primary current.
.48
.44
.40
.36
.32
.28
.24
.20
.16
.12
.08
.04
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 40 50
Primary velocity in volts.
1
2
3
4

Fig. 4. Secondary electron curves for crystalline copper and evaporated copper films.

target for 45 min., a coat of copper being deposited that was practically opaque to visible light. After heating the target in this condition at dull red heat for one min., curve 3 was obtained and curve 4 after 10 min. of heating. The copper disk had been thoroughly outgassed before the target was exposed for deposit and during the deposition the pressure was probably less than 10^{-7} mm of Hg, as the McLeod gauge showed no reading. A curve similar to curve 2 was obtained during preliminary runs when the copper disk was not thoroughly outgassed before the depositing. This makes it probable that the difference between curves 1 and 2 is not due to gas brought down with the metal and this conclusion is further supported by the fact that gas should be more easily re-

moved by further heating than is indicated by curve 3. Also, the effect of outgassing in other experiments has been to decrease the secondary current, while exposing to gas again increases it. It appears more likely that the different results are due to difference in structure, the crystalline surface being covered by evaporation, with an amorphous layer which is subsequently removed or changed over into crystalline form with further heating.

This idea is further supported by some observations taken after heating another copper target at various temperatures and exposing to air at various pressures. Curve 1, Fig. 5, is for a copper target before the apparatus had been baked; curve 2 is for the same target after baking

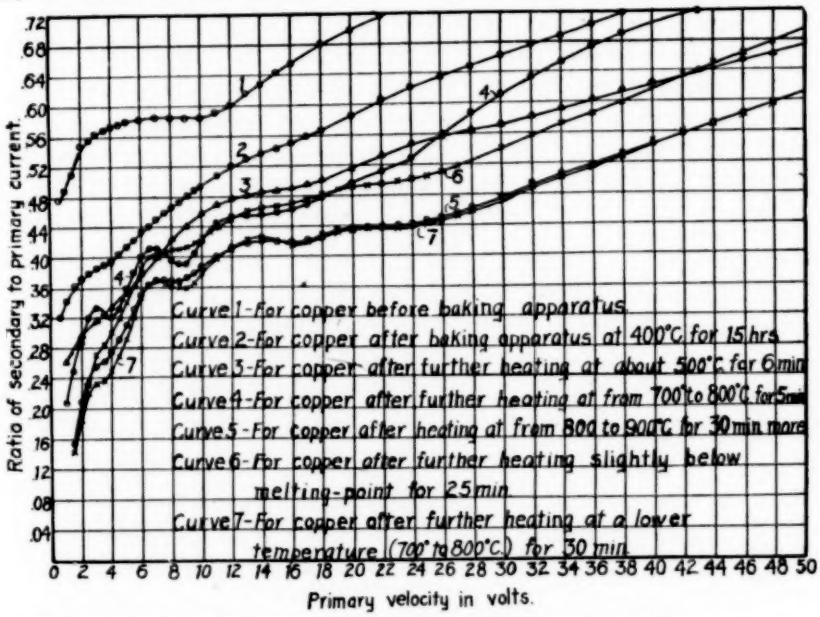
Ratio of secondary to primary current
Primary velocity in volts
Curve 1-For copper before baking apparatus
Curve 2-For copper after baking apparatus at 400°C for 15 hrs.
Curve 3-For copper after further heating at about 500°C for 6 min.
Curve 4-For copper after further heating at from 700° to 800°C for 5 min.
Curve 5-For copper after heating at from 800 to 900°C for 30 min. more
Curve 6-For copper after further heating slightly below melting-point for 25 min.
Curve 7-For copper after further heating at a lower temperature (700° to 800°C) for 30 min.

Fig. 5. Secondary electron curves for copper, showing effect of heat treatment.

the apparatus at 400°C for 15 hours; curve 3 for the target after it had been heated separately at a very dull red heat (just visible in a dark room) for 6 min.; curve 4 for the same target after heating at red heat (somewhat brighter than previously, probably between 700° and 800°C) for 5 min. more; curve 5 for the target after heating somewhat hotter (probably between 800° and 900°C) for 30 min. more; curve 6 for the target after heating at a higher temperature (edges of target melted) for 25 min. more; and curve 7 for the target after heating at a somewhat lower temperature for 30 min. more. After this last heating the target showed a decidedly crystalline appearance which was previously not as noticeable.

These results appear to support the following interpretation. The decrease in the secondary electron current from curve 1 to 3 without appreciable change in the form of the curve, is most likely due to removal of gas from the metal without disturbing the amorphous surface layer. (The target had been simply cleaned with fine emery cloth before assembling the apparatus.) Since the marked change in the form of the curve, as well as an increased secondary current, is produced by further heating at a slightly higher temperature for only a short time, it is obvious that some change has occurred at the metal surface. The time of heating required to effect this change is so short that little change in gas content would occur, and since it depends on temperature rather than on time of heating it appears natural to conclude that it is a structure effect such as the replacement of the amorphous surface layer by a crystalline surface layer. The amorphous layer may either be removed or changed over into the crystalline form by the heating, probably the latter, since no evaporation could be detected. The decrease of the secondary electron current to curve 5, with further heating, is then due to further removal of gas. The surface crystals are not visible until after several minutes of heating but the results do not seem to be affected by the size of the crystals. The increase in secondary current, as shown by curve 6, and the tendency toward disappearance of the various maxima would indicate that some further change of structure takes place with heating near the melting point, perhaps changing over into some other crystalline form or more likely to the amorphous form. P. H. Dowling, of this department, while working with copper in another investigation, found that the crystalline surface became less noticeable after prolonged heating near the melting point. Also, recent results of C. H. Desch[4] show that at high temperatures the surface tension is sufficient to cause rounding of the sharp angles of a crystal of gold. It seems likely that a similar change took place in the above case of copper. Since further heating at lower temperature lowers the curve and brings back the maxima we may conclude that this treatment brings back the same structure as that present when curves 4 and 5 were obtained.

Results showing that gas has little effect on the form of the characteristic curve of copper were obtained after exposing the apparatus to dry air at various pressures. The general shape of the curve was not changed even after exposing the target to air at one atmosphere pressure for 15 hours, the only effect being to raise the curve, i.e., to increase the second-

[4] Abstract of paper presented before the British Association for the Advancement of Science, Toronto, Aug., 1924.

ary electron current. It was found that the secondary current after exposing the target to 1 mm pressure of air for 15 hours was nearly as great as after exposing to one atmosphere pressure for the same length of time.

Our conclusions, then, are that the characteristic curve for copper is obtained only when the surface is crystalline[5] and that this curve is little affected by gas content; that the metal brought down by evaporation forms an amorphous layer which persists on the copper surface until heated in a vacuum or removed by some means; that, in other words, the phenomenon observed is an atomic one, whose characteristics are not brought out until the atoms are arranged in definite order in the crystal structure.

It is also possible with the apparatus shown in Fig. 2 to expose the target to radiation from a quartz mercury arc while it is being bombarded with electrons. This was done to see if the atoms could be put into an excited state by the radiation and the electrons thus made more easily removable by bombardment. The radiation passes through a hole in the cylinder C, covered with gauze. The secondary electron curves thus obtained when simultaneously exposing the target to radiation and electronic bombardment, show that the constant photo-electric current was simply added to the secondary electron current, the photo-electric current being about 1 or 2 per cent of the other.

The form of the characteristic secondary electron curve for copper suggests the existence of several critical potentials at which inelastic collisions occur. It will now be shown that if we make a few simple assumptions we will obtain a curve very similar to the experimental one. Assume that the probability that an impacting electron will escape from the metal is a linear function of the energy with which it hits. Assume also that the primaries all have the same velocity and that f is the fraction that make inelastic collisions for velocities corresponding to r volts or above. At r volts this fraction loses all their energy and remains in the metal and the ratio of the secondary to the primary electron current drops suddenly from cr to $(1-f)cr$, where c is a constant. When the energy of the primary electrons is $r+\epsilon$, the electrons which make inelastic collisions will, however, possess an amount of energy after collision equal to ϵ. If all of these electrons escape from the metal the value of the ratio of

[5] An attempt was made to produce a crystalline surface in air by etching and then studying its secondary electron characteristics before it had been heated at red heat, to see if the curve thus far obtained only after red heat treatment could be reproduced. However, the surface appeared oxidized and the crystals contaminated after being kept in a vacuum for a short time so that the results are of no value.

secondary to primary electrons at $r+\epsilon$ primary volts will be the same as it would have been had there been no inelastic collisions, the only difference being that f of the electrons possess an amount of energy equal to ϵ volts. However, if we assume, as in the original case, that of the fraction f, only $c\epsilon f$ are able to escape, then the total number escaping at $r+\epsilon$ primary volts will be

$$c(1-f)\cdot(r+\epsilon) + cf\epsilon = c(r-fr+\epsilon). \tag{1}$$

If there had been no inelastic collisions the number of secondary electrons per primary at $r+\epsilon$ volts would have been

$$c(r+\epsilon). \tag{2}$$

Since the difference between (2) and (1) is cfr, which is constant, the slope of the curve above the potential at which inelastic collisions occur is the same as that of the portion of the curve below this potential, and the vertical distance between the two parts of the curve is given by cfr (see Fig. 6). Also for a primary voltage of $r+\epsilon$ volts, we would expect

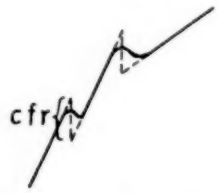

Fig. 6. Theoretical secondary electron curve for crystalline copper.

$c(r+\epsilon)\,(1-f)$ secondary electrons having an energy corresponding to $r+\epsilon$ volts and $cf\epsilon$ having an energy of ϵ volts.

Let $(r+\epsilon)$ increase to a value i (ionization potential) and let F be the fraction of the total number of primary electrons that make inelastic collisions at i volts and lose all of their energy. Let f′ be the fraction of the total number of primary electrons that make inelastic collisions at i volts and lose only r volts energy. f' would be expected to be smaller than f because of the second type of inelastic collisions beginning at i volts. At i volts, then, the ratio of the secondary to the primary current will drop suddenly from $c(i-fr)$ to

$$[1-(F+f')]\,ci+cf'(i-r), \tag{3}$$

assuming as before that the electrons which lose all of their energy stay in the metal. Since the energy of the ionized electrons is also zero they also will remain in the metal. As in the case of the secondary electrons at $(r+\epsilon)$ volts, the slope at $(i+\epsilon)$ will be the same as that at $(i-\epsilon)$ volts if we assume the same constant of proportionality c. If, however, we assume for the ionized electrons a constant of proportionality c' which is

less than c, then the slope of the curve at $(i+\epsilon)$ volts will be correspondingly less than that at $(i-\epsilon)$ volts. If f' is constant above i volts, it will have no effect on the slope of the curve and at most will displace it slightly in the vertical direction.

There is also the possibility of inelastic collisions at the voltages $2r$, $i+r$, $i+2r$, and $2i$ but the number of such impacts would, of course, be expected to be relatively small.

If, as in the actual case, the velocities of the primary electrons have a Maxwellian distribution, then instead of the discontinuities in the curve we would obtain a smoothed over continuous curve as shown in Fig. 6. By properly choosing the values of the constants c, f, c' and F it is seen that a curve is obtained which approximates closely to the experimental curve, at least in the region of the first two maxima. The remaining indistinct maxima of the experimental curve may possibly be accounted for by some of the combinations of successive inelastic impacts mentioned above. These maxima would then be expected to be very indistinct but it is not clear why the secondary current should remain so nearly constant in the region of 15 to 24 volts.

If the above hypothesis is correct, one would expect to obtain evidence of this from the form of the velocity distribution curves. Thus, for example, for a primary voltage somewhat above the first resonance potential one would expect some low-velocity electrons in addition to those having velocities nearly equal to that of the primary beam, the number depending upon the number of inelastic collisions. Since this number is a small fraction of the total number of impacts, as shown by the ratio of f to the ordinate of the curve at that point, one would not expect the evidence of these to be very prominent on the distribution curve. Then too, when one considers the possibilities of a "smoothing over" of any such distribution it is doubtful whether one would obtain experimental evidence of such low-velocity electrons even though inelastic collisions do occur.

Satisfactory results were not secured with the apparatus shown in Fig. 2, but with the apparatus of Fig. 3, specially constructed for the study of velocity distribution, the following results were obtained. The curves shown in Fig. 7 are for copper after it had been heated at red heat for some time. Curves 1, 2, 3, 4 and 5 were obtained with primary velocities of 102, 80, 62, 41 and 21 volts, respectively; curves 6, 7, 8 and 9 with primary velocities of 15, 10.5, 6, and 5 volts, respectively. It will be noted that as the primary voltage is increased above 20 the number of low velocity electrons increases and the number of highest velocity electrons decreases. However, when the primary velocity is as great as 100 volts, 10 per cent of the secondary electrons have

velocities only slightly less than that of the primaries. For the curves 7, 8 and 9, corresponding to the lower primary velocities, it will be noted that there is a distribution similar to that described in the previous discussion. For a primary velocity of 10.5 volts there is a group of secondary electrons present having velocities up to 4 volts indicating a loss of 6.5 volts, which is in good agreement with the second maxima of the secondary electron curve. For a primary velocity of 6 volts, curves 8 and 9 indicate a loss of 2.5 and 3.25 volts, respectively, while the first maxima of the secondary electron curve is at 3 volts. The curves shown

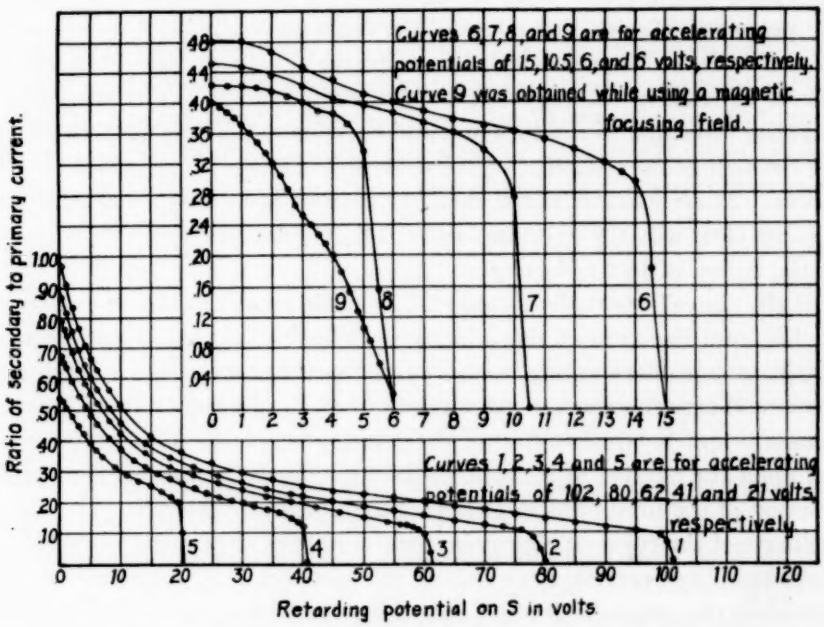
Curves 6, 7, 8, and 9 are for accelerating potentials of 15, 10.5, 6, and 6 volts, respectively. Curve 9 was obtained while using a magnetic focusing field.
Curves 1, 2, 3, 4 and 5 are for accelerating potentials of 102, 80, 62, 41, and 21 volts, respectively.
Ratio of secondary to primary current.
Retarding potential on S in volts

Fig. 7. Curves showing velocity distribution of secondary electrons from crystalline copper.

were selected from a large number and are ones which show this distribution most prominently. These curves could not be reproduced at all times under apparently the same conditions. A great many curves were taken for primary voltages in this region, and several different copper targets of chemically pure copper as well as commercial copper were used. A survey of the results indicates that curves similar to curves 8 and 9 were obtained about 50 per cent of the time, while the others are smooth curves with no visible breaks. Curve 7 is more easily reproducible. This might be expected since the second maxima of the secondary electron curve is much more prominent than the first.

Various attempts were made to determine the reason why the above curves could not always be reproduced, but without success. Curve 9 was obtained with a magnetic field in the direction of the primary stream of electrons and indicates a smaller percentage of higher velocity electrons than without the field. This may be due to a change in the direction of the secondary electrons resulting in the measurement of only one component of velocity. The other curves were obtained with no magnetic field present. It was found necessary to apply the retarding potential to both the sphere *S* and the cylinder *C* (see Fig. 3) so as to keep the potential between *S* and *C* constant. Actually *C* was kept 3 volts positive with respect to *S* at all times. This was necessary to keep the primary electron stream from spreading.

If the various maxima in the secondary electron curve and the breaks in the velocity distribution curves of the secondary electrons are due to the same cause, one would expect, of course, that they should be reproducible with equal accuracy. The only explanation seems to be that the secondary electron curve is obtained under conditions of constant potential difference between the target and sphere while this potential difference is continually being varied during the observations on velocity distribution. It may be that this procedure, necessary for measurements on velocity distribution, is effective in producing a condition which is very critical for velocity measurement of secondary electrons. The results do not appear characteristic of the apparatus since they were observed with two different types (see Figs. 2 and 3).

As previously mentioned, the ratio of secondary to primary current could also be obtained with the apparatus shown in Fig. 3. This was always done before making measurements on velocity distribution of secondary electrons to make sure that the characteristic curve was obtained. In one instance a copper target was mounted at an angle of 45° with the primary electron stream. The magnitude of the secondary current for primary velocities below about 50 volts was found to be about the same as for perpendicular incidence. For higher primary velocities the secondary current is greater than for perpendicular incidence. At 250 volts primary velocity, the ratio of secondary to primary current was found to be 1.35 for 45° incidence and 1.14 for perpendicular incidence. The shape of the secondary electron curve for 45° incidence is similar to the one previously obtained for perpendicular incidence except that the first two maxima are much less prominent.

V. Results for Magnesium and Aluminum

Since the inelastic potentials for magnesium in the vapor state have been experimentally determined, it was thought worth while to see if any indications of such could be obtained in the solid state. Fig. 8 shows the secondary electron curve for magnesium after it had been heated somewhat below the melting point by high frequency induction so that the surface had evaporated. The surface appeared very rough but there were no visible crystals present. It will be noted that there are no prominent maxima such as were observed for copper. The curve

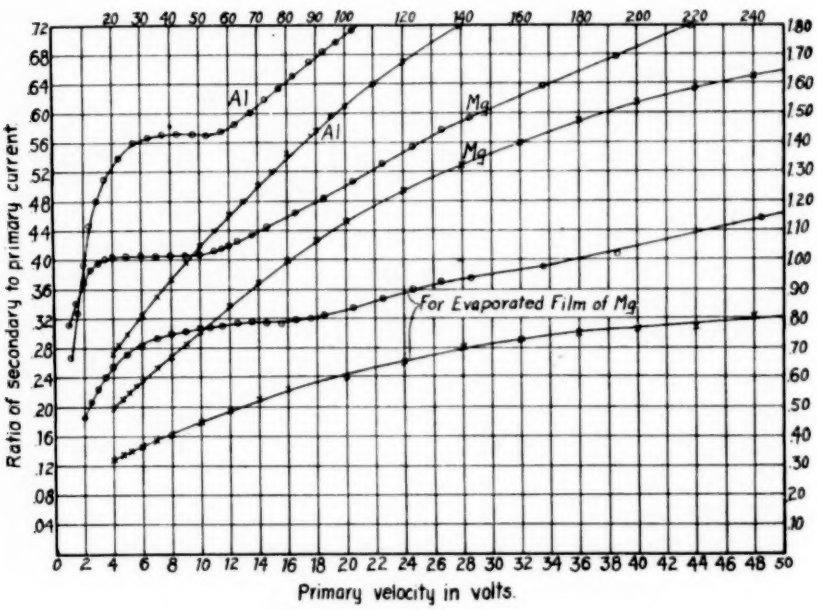

Fig. 8. Secondary electron curves for Al and Mg.

resembles more closely the one originally obtained for nickel, with the sudden increase coming at 11 volts instead of 9 volts. Measurements of velocity distribution of secondary electrons indicate that there are a few low velocity electrons present for primary velocities as low as 11 volts. A curve is also shown which was obtained after magnesium had been evaporated onto the target. Here, as also with copper, the effect of an evaporated film is to decrease the secondary current very much.

A curve for aluminum is also shown in Fig. 8, which was obtained after heating the target somewhat below the melting point by high frequency induction. The velocity distribution of secondary electrons from aluminum was found to be similar to that of magnesium. The unique feature

of the curves for Al and Mg is the extraordinarily large secondary current in comparison with that for the other metals studied. The secondary current was increased somewhat by the heating. The curves marked with crosses are plotted to the scale at the right and top of Fig. 8.

VI. Concluding Remarks

The reason why the characteristic secondary electron curve for copper should possess such prominent maxima when the curves for the other metals do not, is not at all clear. The fact that copper is the only one of the metals investigated which became visibly crystalline may be the determining factor. Since copper apparently has a rather limited temperature range at which crystals are formed, this would also be expected to be true for the other metals. Hence it may be that the temperature at which the other metals were heated does not lie within this range. This indicates the desirability of a more detailed study of the effect of heat treatment on other metals in the attempt to find a temperature at which surface crystalline characteristics will be developed.

The values of the accelerating potentials of 3.0 and 6.5 volts, at which evidence of inelastic collisions for crystalline copper was obtained, are lower than the values 3.8 and 7.69 volts, respectively, given by Foote and Mohler for the inelastic potentials of copper in the vapor state. However, it appears reasonable that the inelastic potentials of atoms when arranged in a crystal lattice should be different from those of the same atoms when separated from one another.

National Research Fellowship,
The University of Wisconsin,
Madison, Wisconsin.
August 30, 1924.

THE EFFECT OF SURFACE CHARGES IN VACUUM DISCHARGE TUBES

By A. R. Olson and T. F. Young

Abstract

Current-voltage curves obtained with a four electrode tube with two rather widely separated gauzes, showed discontinuities at voltages which were evidently not critical potentials since they varied with the gas pressure. Since charges on the glass surface were thought to be responsible, *a simple case was studied*. Electrons were accelerated from a filament through two gauzes, 3.3 cm apart and held at the same potential, to a plate, the space between the gauzes being surrounded by a metal cylinder C insulated from both. This cylinder became negatively charged until the loss or leak just equaled the gain due to the faster electrons. As the accelerating voltage A_1 was increased, a value b was reached at which both the voltage of C and the current suddenly increased greatly, and these larger values were maintained until A_1 was decreased to a limit a, considerably lower than b. A study of the equipotential surfaces gives an explanation of these effects. The discontinuities may be eliminated by controlling the voltage of the cylinder C. In experiments in which electron velocities must be known, it is evidently necessary that insulated "floating" surfaces be avoided and that the potential of all parts of the wall be controlled.

IN numerous published researches on the critical potentials of gases, discontinuities in current-voltage curves have been obtained. Horton and Davies[1] obtained such discontinuous curves in their work on argon and Foote and Mohler[2] described similar results in their work on nitrogen. Working with oxygen, we have observed discontinuities in our curves, which are similar to those mentioned above. However, in our work, increased pressure caused the discontinuities to occur at lower voltages, whereas, in other work pressure had either no effect or the opposite effect. In Fig. 1 we have reproduced curves obtained in the preliminary work with oxygen. Each discontinuity, it appeared, could be explained by ascribing it to some combination of the published values of the critical potentials of this gas, yet such an explanation was not tenable when it was found that the positions of the breaks could be made to vary continuously by gradually changing the pressure. Moreover, it did not seem probable that the discontinuities could be explained, as may sometimes be done, by assuming the breaking down of a large space charge, for the currents used were about 10^{-7} ampere. There was, however, the

[1] Horton and Davies, Proc. Roy. Soc. A97, (1920)
[2] Mohler and Foote, Bur. Stds. Sci. Papers, No. 400, 1920

possibility that a surface charge, such as Elster and Geitel[3] found in their work on the photo-electric effect, might accumulate on the glass walls of the tube and exert an influence on the electron stream passing near it.

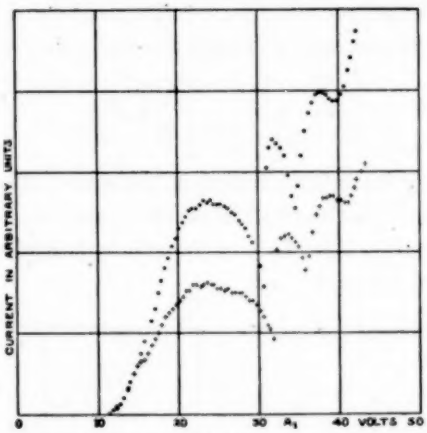

Fig. 1. Spurious discontinuities observed in oxygen.

Apparatus

The ionization tube used in the investigation described below, which is similar to others frequently employed in work of this kind, is shown in diagram in Fig 2. To determine the existence or non-existence of a surface charge, a cylinder made of copper was substituted for the glass walls

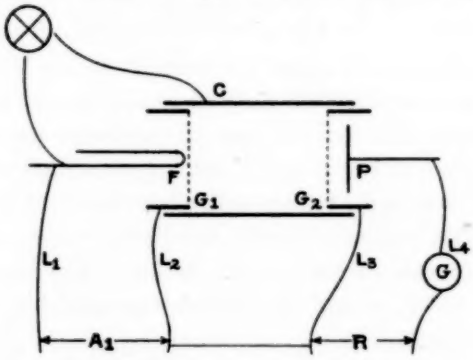

Fig. 2. Diagram of ionization tube and connections.

used in the work described above. At each end of the copper cylinder but insulated from it, were two platinum gauzes G_1 and G_2, forming an ionization chamber 3.3 cm long and 2.6 cm in diameter. The potential of the cylinder could be measured with respect to one of the leads of the

[3] Elster and Geitel, Phys. Zeit. **14**, 741 (1913)

oxide-coated platinum filament F, by means of a potentiometer and quadrant electrometer. Electrons were accelerated from F to G_1 by a variable potential which we will call A_1. A low resistance galvanometer G is shown at its normal position L_4 but it could be shifted easily to L_1, L_2 or L_3, in order to measure the currents from the filament or from the gauzes.

Experimental Results

In Fig. 3 we have plotted as a function of the potential A_1, the measured values of the current to the plate (Curve I) and of the potential of the copper cylinder (Curve II). In this experiment, hydrogen at a pressure of about 0.1 mm of Hg was used.

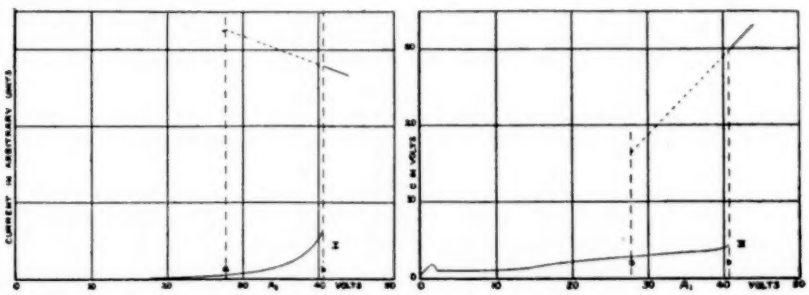

Fig. 3(I). Current to the plate P as a function of A_1.
Fig. 3(II). Potential of copper cylinder c as a function of A_1.

Every value of A_1 to the left of the line a, determined unique values of the cylinder potential and of the current to the plate, which were attained regardless of whether A_1 was increased or decreased to that point. At b both the current and the cylinder potential increased abruptly. Decreasing A_1 through b did not restore either the current or the cylinder potential to its former value, but they followed in the general direction of the dotted curves until the line a was reached when they changed suddenly to the solid curves. When A_1 was increased beyond b, the current to the plate and the cylinder potential were again single-valued functions of A_1.

With A_1 between a and b, the current to the plate and also the cylinder potential could be made to assume values on either the solid or the dotted curves, according to whether the cylinder potential was made to assume momentarily a value in the neighborhood of the one curve or the other. Either of these conditions could be maintained indefinitely, but in no case did we obtain any other condition if the cylinder potential was left free to vary.

Discussion of Results

In order to understand clearly the conditions within the cylinder, it was desirable to know the potential at various points within this space. Since the two gauzes were kept at a known potential and since the potential of the cylinder was measured, such a calculation was easily made.[4] A cross section of certain calculated equipotential surfaces is mapped in Fig. 4. The difference between adjacent equipotential lines is one tenth of the potential difference between the cylinder and the gauzes. The potential on the .5 line, for example, is equal to the potential of the gauzes plus one-half the difference in potential between the gauzes and the cylinder.

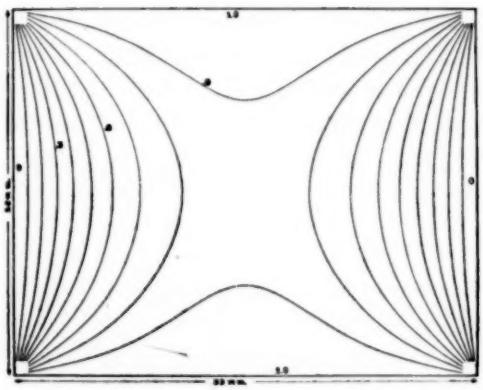

Fig. 4.

It will be seen from Fig. 4 that if an electron enters the space through the gauze G_1, it encounters a retarding field, due to the surface charge on the cylinder, until it reaches a point midway between the two gauzes. From there on it is accelerated, reaching G_2 with its original velocity if no impact has taken place. Those types of impacts such as ionization which can occur only when electrons have velocities exceeding a certain minimum value, must be confined to two regions near the gauzes. The extent of these regions depends upon the amount that A_1 exceeds the critical voltage and upon the potential of the cylinder. For example, if electrons pass through the gauze G_1 after having acquired a velocity equivalent to 30 volts, they can ionize hydrogen only as long as they have lost less than 14 volts velocity, for approximately 16 volts is necessary to ionize this gas. If the potential of the cylinder differs from that of the

[4] Byerly, Fourier's Series and Spherical Harmonics, p. 232, Ginn and Co., 1893. Anding, Sechsstellige Tafeln der Bessel'schen Funktionen Imaginaren Argumentes, Engelmann, Leipzig, 1911.

gauze by 23 volts, then ionization can occur only in the volumes bounded by the gauzes and the .6 lines, Fig. 4. In the following discussion we refer to the maximum width of these ionization (or resonance) regions (which can be estimated from Fig. 4) as T.

When a stream of electrons passes through the gauze G_1 after falling through the field A_1, their directions are changed due to mutual repulsions and to collisions or interactions with gas molecules. Some of the electrons reach the cylinder and build up a charge upon it which is negative with respect to the gauze. This charging would continue until the potential built up would be sufficient to repel the fastest electrons if there were no opposing factors. However, due to leakage across the insulators, to photo-electric emission from the cylinder, to positive ions reaching the cylinder, and to "splashing"[5] of electrons from it, the potential that the cylinder acquires is less than that corresponding to the fastest electrons. The potential reached is that at which a dynamic equilibrium exists between the electrons reaching the cylinder and those leaving it.

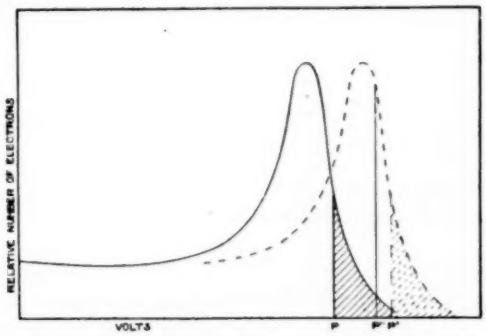

Fig. 5. Distribution of electron velocities.[6]

Let Fig. 5 represent the distribution of velocities of the electrons[6] for some single value of A_1. If P is the potential of the cylinder with respect to the gauze, then electrons with velocities greater than P can reach the cylinder. The number of electrons with velocities sufficiently high is represented by the shaded area under the curve to the right of P, and these, minus those whose energy is diminished by collisions must just neutralize the "leak." If A_1 is increased to A_1' so that the dotted curve represents the distribution of electron velocities, the "leak" from the cylinder is increased and more electrons are required to reach it. Hence

[5] Barber, Phys. Rev. (2) **17**, 322 (1921)
[6] Goucher, Phys. Rev. (2) **8**, 566 (1916);
Pawlow, Proc. Roy. Soc. **90**, 398 (1914);
Congdon, Phil. Mag. **47**, 458 (1924).

P does not move to a new position P' so that the shaded area to its right is equal to the former value, but moves only to P''. The difference between P' and P'' is equal to the change in cylinder potential C measured with respect to the filament. This difference between the potential of the cylinder and the filament is controlled by electrons leaving the cylinder and those reaching it. Since some may be prevented from reaching it because of ionizing collisions and since ionization increases the "leak" from the cylinder, the potential difference C is a function of the volume in which ionization can take place. In other terms it is a function of the maximum width T of the ionization regions,[7] which can be estimated from the measured value of the cylinder potential with the aid of the plot in Fig. 4. The dependence of C upon T is exhibited by the solid curve I, Fig. 6.

We can use this curve to determine the rate at which C would increase with T, but to determine the way in which T depends upon the value of C is another problem. By the aid of the map, Fig. 4, we can calculate T for any series of values of C when A_1 is constant. The dotted curves in Fig. 6 illustrate the dependence of T upon C for several values of A_1, as parameter.

When A_1 is increased by a small amount, an increase in the volume of ionization results. Since C is a function of the volume of the ionization region T as expressed by the solid curve Fig. 6, C increases also. T is simultaneously determined by C according to curve II, Fig. 6 (drawn for the new value of the parameter A_1). Hence the values which C and T assume are those at the intersection b of the two curves.

If A_1 is further increased, T and consequently C continue to assume larger values. A given change produced in one has a larger and larger effect upon the other, as is evident from the changing slopes of the curves. Eventually a point is reached such that any increase in T produces a change in C so large that the reciprocal effect upon T is larger than the original variation. This condition arises when the solid and dotted

[7] What is here said applies most simply to electrons having the single velocity A_1. It applies similarly to those with higher and lower velocities but for them the volume of the ionization regions are larger or smaller respectively than the regions indicated by T. However, these regions increase as T increases (due to variation in A_1 etc.) and T may be considered a function of the average volume in which all the electrons may ionize the gas. An application of the Kinetic Theory of gases, together with the curve for the distribution of electron velocities might determine completely the manner in which T determines C. Such a study would have to take account also of the possibility of two collisions by one electron and relations might have to be determined for various values of A_1 as a parameter. We will assume the simple relation expressed by the solid curve of Fig. 6 for the purpose of this qualitative discussion.

curves become tangent and is, of course, unstable. Consequently a large change suddenly occurs in T, resulting in a value so large that ionization may fill the whole tube. Since the extent of the influence of C and T upon each other continues to increase during these changes, the value of C after the sudden large increase is considerably larger than is necessary to maintain ionization throughout the whole volume of the tube. Hence if A_1 is decreased, T may not do so until A_1 has reached a considerably lower value. Eventually T may begin to decrease and by means of phenomena similar to those described above, a second discontinuity may result as the cylinder potential leaves the dotted curve (Fig. 3) and assumes values on the solid curve. It might be predicted that between the points a and b, the cylinder potential could be made to assume stable

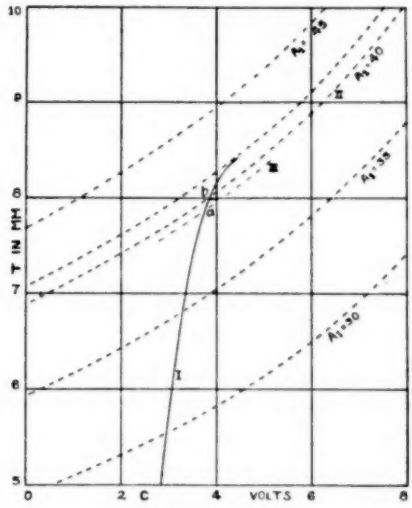

Fig. 6.

values on either curve. The experimental confirmation of this we have already mentioned.

The relation of the cylinder potential to the current through the tube can now be considered. A high negative charge on the cylinder drives back many electrons having velocities too low to overcome its retarding influence. Hence when the cylinder potential drops from a large negative value with respect to G_1 to a much smaller value, many slow speed electrons previously turned back toward G_1 are now able to reach the second gauze G_2 and the plate.

A large retarding field (for electrons) between the gauze G_2 and the plate enabled the positive ions reaching the plate to be studied separately. The number reaching the plate was found to be considerably decreased when

the cylinder potential suddenly assumed a less negative value. This was probably due to the fact that at high pressures of the gas the electrons were removed so thoroughly in the part of the tube near the first gauze that few were left to produce ions at the second gauze. The effect was more pronounced with increase in pressure, and at high pressures the positive ion current dropped almost to zero.

The larger number of collisions at higher pressures results in a greater rate of change of C with increase in the volume of ionization. This means that the curves of Fig. 6 change slope more rapidly and become tangent at lower values of A_1. Consequently the discontinuity in the cylinder potential and the resulting changes in the number of electrons and ions reaching the plate occur at lower values of the accelerating potential A_1 when the pressure is increased.

It is very significant that no discontinuity in the current passing through the tube was found when the cylinder was held at a constant potential and A_1 was increased to very large values. The change in cylinder potential is evidently, then, the primary cause of the discontinuous phenomena within the tube. Were an ordinary space charge or increased emission from the filament responsible, a sudden change in the current should result even if the cylinder is held at constant potential, providing at least that such a potential is near its natural value just before the break. This reasoning is substantiated by the fact that the algebraic sum of the changes in current to the two gauzes and to the plate was found to be zero. It is further to be noted that there is some quantative support for our postulate in the fact that the discontinuities appeared very close to the values which one would predict from inspection of the curves in Fig. 6.

The close similarity of these breaks to those obtained before the glass cylinder was replaced by one of copper is strong evidence that glass also can hold a surface charge under these conditions. It is important, therefore, to shield all of the glass surfaces in an electron tube in which conditions must be accurately known, or to so construct the tube that corrections can be determined for the surface charges residing on the glass or other insulated surfaces. We have shown how this can be done in one instance.

This research was begun while the first author was a National Research Fellow in chemistry. We take this opportunity for expressing our appreciation to the National Research Council.

UNIVERSITY OF CALIFORNIA,
June 4, 1923.

ON SOME PROPERTIES OF NEON TUBES

By B. N. Ghose

Abstract

Osglim neon glow lamp.—*The current* through the tube is intermittent, the frequency being in the audible range if sufficient resistance (10 megohms) is placed in series. No current flows unless the applied voltage lies between two critical values. The *voltage drop* through the lamp, the product of the current and resistance as measured with d.c. instruments, is independent of the current and is approximately equal to the mean of the two critical voltages. The *light intensity* is directly proportional to the current.

Use of Osglim lamp to measure high resistances.—From the ratio of the light intensities of the lamp when in series with a known and with an unknown resistance, the latter may be determined. The method is quick and easy.

Introduction

QUITE a large number of experiments have already been made upon the neon tubes manufactured by the General Electric Company under the trade name "Osglim." The current voltage characteristic of the lamp as determined by Pearson and Anson[1] shows that the lamp has a negative resistance, i.e. the resistance of the lamp increases as the current passing through it decreases. It has also been observed that there is a critical voltage below which the lamp does not glow. No current passes through the lamp while it is not glowing. But if the applied voltage is just greater than the critical voltage the lamp will glow even if the resistance in series with the lamp be so great as to reduce the current to only a fraction of a microampere. The intensity of light of the lamp however also decreases with the current passing through it.

The fact that the tube possesses an upper and a lower critical voltage (as shown by Pearson and Anson) together with the fact that it glows when the e.m.f. is greater than either critical voltage even with a large resistance in series, shows that the current through the lamp is of a pulsating nature. When the current starts in the tube there is a fall in voltage across its electrodes below the lowest critical voltage on account of the large resistance in series. This stops the current and the process is repeated. As the condenser capacity of the tube is very small the frequency of pulsation is beyond the audible limit when the series resistance is small but with a resistance of 10 megohms the pulsation can be heard by inserting a telephone in series.

[1] Pearson and Anson, Proc. Phys. Soc., **34**, pp. 175, 204 (1922).

It has also been observed by Watson[2] that the current through a neon tube is intermittant when the anode is in the dark space and the current density is low. The whole of the light from these tubes comes from the negative glow,[3] the electrodes being so close together that the positive column is absent.

While there is very little use in making any general research on a commercial article such as a glow discharge lamp, it is interesting to know if such lamps may be used for the measurement of some physical quantities. In this paper, therefore, an attempt has been made (1) to determine the law of variation of the effective resistance of the lamp with the current passing through it; (2) to investigate the relation between the intensity of light from the lamp and the current passing through it; and (3) to determine a method of measuring very high resistance by the help of the above two investigations.

1. *Determination of the law of variation of the effective resistance of the lamp with current.* The resistance inside the cap of the lamp and connected in series with it was taken out and the lamp was connected in series with a milliammeter, a variable resistance and a source of direct current. Three sets of observations were taken with three different tubes and the results are shown in Table I where C is the current through the lamp and R is the effective resistance of the lamp. It is evident that the voltage drop $CR=K$ is approximately constant. It increases somewhat with the applied voltage, and is roughly equal to the mean of the two critical voltages of the lamp.

TABLE I

Resistance as a function of current for neon lamps

(a) Voltage 175-180			(b) Voltage 220-226			(c) Voltage 233-238		
C (10^{-3} amp.)	R (10^3 ohms)	CR (volts)	C (10^{-3} amp.)	R (10^3 ohms)	CR (volts)	C (10^{-6} amp.)	R (10^6 ohms)	CR (volts)
6.1	28	171	8.4	20	168	24.5	7.4	181
4.2	37	155	7.0	24	168	24.0	6.9	166
3.6	44	158	6.0	27.5	165	15.0	11.7	175
2.8	55	154	4.0	40	160	11.8	16.2	191
1.8	83	150	2.0	80	160	9.0	18.9	170
1.5	93	140	1.5	108	162	8.0	22.8	182
0.8	187	150	1.0	187	187	7.0	25.4	178
	Mean:	154		Mean:	165		Mean:	178

2. *Determination of the relation between the intensity of light of the lamp and the current passing through it.* Two of the lamps experimented upon were enclosed in two wooden boxes, each having a rectangular aperature on one side. The cathode of each lamp faced the aperture, which was

[2] Watson, Proc. Camb. Phil. Soc. **17**, 102

[3] Ghose, Nature, December 29, 1923, p. 944

big enough to allow all the light from the cathode to fall on the screen of a Lummer-Brodhun photometer head. The two lamps were mounted at the ends of an optical bench with the photometer between.

Lamp No. 1 was connected in series with a resistance of 5000 ohms and lamp No. 2 in series with a variable resistance (5000 to 60,000 ohms) each having a milliammeter in series and being connected to the d.c. supply mains. The intensities of light emitted by these lamps were compared by adjusting the photometer head, and the corresponding current in each circuit was recorded.

OBSERVATIONS

Current in lamp No. 1 kept constant at 15.0×10^{-3} amp.						
Current in No. 2, $C_2(10^{-3}$ amp.) :	6.00	3.50	2.30	1.25	1.00	0.90
Ratio C_1/C_2 :	2.50	4.28	6.52	12.0	15.0	15.8
Ratio of intensities I_1/I_2 :	2.57	4.22	6.30	12.1	14.5	15.9

The observations show that the ratio of the intensities is equal to the ratio of the currents.

3. *Determination of a high resistance with a neon lamp.* Let C_1 be the current through lamp No. 1 having a resistance r_1 in series, and C_2 be the current in lamp No. 2 having a resistance r_2 in series. Also let R_1 and R_2 be the resistances of the lamps for the currents C_1 and C_2. Then

$$C_1R_1=C_2R_2$$

Also

$$C_1(R_1+r_1)=C_2(R_2+r_2)=E$$

where E is the voltage of the d.c. main.

Hence

$$R_1/R_2=(R_1+r_1)/(R_2+r_2)$$

or

$$R_1/R_2=r_1/r_2=C_2/C_1=I_2/I_1.$$

Hence for known values of r_1, r_2 can be found from the above equation by measuring I_1/I_2. This gives a method of measuring high resistances of the order of a few megohms by means of a neon lamp.

A number of determinations of high resistances have been made by this method and the results in two cases are as follows.

This quick and easy method of determining high resistances may be useful to the radio experimenters.

	Case 1	Case 2
Resistance r_1 in series with No. 1 :	5,000 ohms	80,000 ohms
Resistance r_2, calculated from measured I_1/I_2:	79,500 ohms	2.04×10^6 ohms
Resistance r_2 determined by ballistic galv. :	80,000 ohms	2.02×10^6 ohms

In conclusion the author wishes to express his thanks to Dr. Wali Mohammad for his assistance with valuable advice and useful suggestions.

PHYSICS DEPARTMENT, LUCKNOW UNIVERSITY, LUCKNOW, INDIA.
September 11, 1924.

MOBILITY OF NEGATIVE IONS IN FLAMES BY THE HALL EFFECT METHOD

By J. S. Watt

Abstract

Variation with potential gradient of mobility of negative flame ions.—Using a flat salted flame, previously described by Wilson, between the poles of an electromagnet giving a field of 5000 gauss, the horizontal potential gradient X due to the current sent between two Pt electrodes and also the vertical potential gradient Y due to the Hall effect, were measured by means of two Pt sounding wires which could be rotated about a horizontal axis and which were connected to a quadrant electrometer. For a *flame containing potassium carbonate* the mobility $k_2 = Y/HX$, was found to decrease from 26 m/sec for 1 volt/cm when the potential gradient was 1 volt/cm, to 16 m/sec for a gradient of 30 volts/cm. For a *flame free from salt* the mobility was somewhat greater, decreasing from 26.5 m/sec for 5 volts/cm to 16 m/sec for 50 volts/cm. However, wide variation of concentration produced so little effect on the mobility that it could not be detected with certainty. The magneto-resistance effect which Heaps[1] has shown enters into the mobility equation, was so small as to be negligible.

Asymmetry of the Hall effect in flames.—The Hall effect was found to vary slightly with the direction of the magnetic field, the asymmetry being greater the greater the amount of salt in the flame. This asymmetry was probably due to the effect of the magnetic field on the upward velocity of the flame gases, which was evident in these experiments.

THEORIES developed in the last few years indicate that the mobility of electrons in gases depends on the strength of the electric field in which they move, and that the mobility decreases as the potential gradient increases.[2] The purpose of the work described in this paper was to determine the variation of the mobility of negative ions in a flame with the potential gradient across the flame and with the concentration of the salt solution sprayed in. The experimental method used was the Hall effect method.

Marx in 1900[3] found that the Hall effect diminished as the concentration of the salt in the flame increased. In 1914 Wilson[4] found that the mobility of the negative ions did not vary with the concentration of the salt solution sprayed into the flame, and was also independent of the kind of salt used. He thought that there was no variation of mobility with

[1] C. W. Heaps, Phys. Rev. **24,** 652 (December 1924)
[2] K. T. Compton, Phys. Rev. **22,** 334 (1923)
[3] Marx, Ann. der Phys. **1,** 790 (1900)
[4] H. A. Wilson, Phys. Rev. **3,** 375 (1914)

potential gradient, but made no detailed investigation. The value of the mobility found by Wilson was 2450 cm/sec for 1 volt/cm.

Bryan and Wilson[5] determined the mobility of negative ions in a flame by considering the conductivity of a flame for rapidly alternating currents. Their results showed a variation of the mobility with the potential gradient and with the concentration of the salt sprayed into the flame. When a solution of 1 gm of potassium carbonate per liter was used they found with potential gradients of 64 and 9 volts/cm mobilities of 61 and 193 m/sec, respectively, for 1 volt/cm. The discrepancy in the absolute values found by the two methods is not understood.

Apparatus and Experimental Procedure

The apparatus used in this work was the same as used by Wilson in his investigation of the Hall effect.[4] The burner consisted of a brass tube into which a row of twelve quartz tubes was cemented. The use of quartz served to insulate the flame. Into this burner was led a mixture of gasoline and air, into which salt solution had been sprayed. The resulting flame was about 13 cm long, 7 cm wide and 2 cm thick. The usual pressure regulators were used to obtain a steady flame. An electric current could be sent horizontally through the flame between two platinum gauze electrodes kept red hot by the flame. A water cooled Weiss electromagnet with flat pole pieces 10 cm in diameter and 4.65 cm apart was used to produce the magnetic field in the flame, the strength of the field obtained being measured by means of a fluxmeter.

The Hall effect angle was determined by means of two insulated platinum wires a short distance apart, which were inserted in the flame through the center of one of the pole pieces and connected to a well insulated quadrant electrometer. To make the Hall effect easier to measure, potassium carbonate was placed on one electrode which was accessible, and lime on the other, because its position would not allow a frequent replenishing of the supply. The method used made first one electrode and then the other the cathode.

The experimental procedure was as follows. The flame was adjusted until it reached a steady state. With a current flowing through the flame and the magnetic field on, the measuring wires connected to the electrometer were turned until the electrometer showed no deflection. Then the magnetic field was reversed and the wires turned until the electrometer again showed no deflection. One half of the angle turned through gave the Hall effect angle θ. By the ordinary Hall effect theory, we have

[4] Bryan and Wilson, Phys. Rev. **23**, 195 (1924)

tan θ equal to the average value of Y/X for the two directions of the magnetic field, where Y is the vertical electric field appearing after the magnetic field is put on and X is the horizontal electric field

In order to measure the potential gradient at the point where the Hall effect was obtained it was necessary to know the sensitivity of the electrometer. This was found to be about 100 mm per volt, but the value changed from time to time so that the electrometer was tested before each day's work. If the sensitivity had changed the instrument was recalibrated.

To measure the potential gradient the wires connected to the electrometer were used. With the magnetic field zero, these wires were turned until the electrometer deflection was zero, then they were turned through some angle ϕ and the electrometer deflection observed. Knowing the sensitivity, the voltage V necessary to give this deflection could be found; and if d was the distance between the wires, then $V/(d \sin \phi)$ gave the potential gradient in volt/cm. The angle ϕ was often small, especially when the potential gradient was large, but the values obtained in the above manner were checked against those obtained with a less sensitive electrometer where ϕ could be made 90 degrees. The agreement was within experimental error.

Two methods of varying the potential gradient X were used. In the first, the current through the flame was reversed. Since the electric field in the flame was not symmetrical the potential gradient changed at the point where the measurements were being made. The change was usually not very large. The other method was to vary the voltage across the flame. The two methods were frequently combined.

It was observed that reversing the direction of the magnetic field caused the flame to alter very much in appearance. When a current of about 40 milliamperes flowed through the flame, a magnetic field of about 5000 gauss would very obviously slow up or increase its vertical motion. The theoretical aspects of this phenomenon are considered by C. W. Heaps in a recent paper.[1]

It was found that the Hall effect varies slightly with the direction of the magnetic field, the variation being greater the greater the concentration of the salt sprayed in. When solutions of small concentration were sprayed into the flame, the variation could hardly be detected, but with a highly concentrated solution it became very noticeable.

In the paper by Heaps the theory of the change in the character of the flame with the magnetic field is considered and the following formula for the Hall effect derived

$$Y/HX = (k_1 - k_2)/(1 + \Delta)$$

where H = magnetic field,

X = horizontal electric field,

Y = vertical electric field,

k_1 = mobility of positive ions,

k_2 = mobility of negative ions,

Δ = magneto-resistance effect, or fractional increase of resistance of the flame when the magnetic field is put on.

In the formula above, Δ must be determined for the same direction of H as was used when Y/HX was measured. Suppose we neglect k_1 with respect to k_2, then

$$k_2 = -(Y/HX)\ (1+\Delta) = -M(Y/HX).$$

The procedure was to take the average value of Y/HX and also of Δ for both directions of H.

To obtain data for the calculation of M the following method was employed. With the magnetic field equal to zero, the wires connected to the electrometer were turned so that the electrometer showed no deflection. Then they were turned through some known angle and the electrometer deflection noted. Next the magnetic field was put on in one direction, the wires adjusted to a new zero position and then turned through the same angle as before, and the electrometer deflection noted. The magnetic field was then reversed and the process repeated. Since the sensitivity of the electrometer, the current through the flame, and d, the distance between the wires, were known, the resistance of the flame in each case could be calculated and hence Δ. The results are given in Table I, where Δ_1 and Δ_2 are the two values obtained for the opposite directions of H. Δ_2 always corresponded to a decrease of resistance.

TABLE I

Observations for a field of 4000 gauss

X	Δ_1	Δ_2	M	N
4.9 volts	0.120	−0.127	0.985	10
30.4	0.136	−0.154	0.982	10
5.2	0.161	−0.171	0.973	8
14.8	0.165	−0.211	0.966	8
16.4	0.228	−0.258	0.974	7
6.1	0.152	−0.153	0.977	7

Each value is the average of N trials, the value of X in each trial being in the neighborhood of the average value given.

For these experiments then, M was very nearly unity. Since the values of the mobility are probably not accurate to better than five per cent, it is evidently not worth while to apply the correction factor M.

Results

The results are given in the following tables. The first column gives the range of potential gradient for the N trials, for which the second and third columns give the average values of the potential gradient and mobility.

Table II

Variation of mobility of negative ions with potential gradient in a salted flame

Range of X (volts)	Mean X (volts)	k_2 (cm/sec)	N
0— 1	0.76	2640	16
1— 2	1.63	2560	25
2— 3	2.50	2420	26
3— 4	3.54	2170	37
4— 6	5.35	2030	75
6— 8	7.00	2010	56
8—10	9.30	1860	20
10—12	11.0	1750	19
12—14	13.0	1700	32
15—25	20.2	1660	30
25—35	31.9	1580	33

In this table all of the data for flames containing potassium carbonate are averaged together regardless of the concentration of the solution because changes of concentration produced very little effect on k_2. For very low values of X, two values of k_2 were obtained which were very low. These values were rejected, since for such low values of the potential gradient some factor might enter which under ordinary conditions would not affect the results. Below a certain value of the potential gradient results were erratic and unreliable because of experimental difficulties.

In Table III the results obtained for a flame free from salt are given.

Table III

Mobility of negative ions in a flame free from salt

Range of X (volts)	Mean X (volts)	k_2 (cm/sec)	N
3— 6	4.9	2660	19
8—16	12.7	2140	13
16—24	20.2	2000	12
24—43	37.8	1780	11
50—55	51.5	1570	5

These results show that k_2 decreases steadily as the potential gradient increases. This decrease is also shown by the individual measurements, for whenever a measurement was taken after increasing the electric field, it was found with very few exceptions in 400 observations, that the Hall effect angle had decreased. In Fig. 1 the data from the two tables are plotted. The curves quite obviously show a smaller mobility with the

salt than without. The effect is small, however, and the differences for different concentrations were so small that they could possibly be explained as due to experimental error.

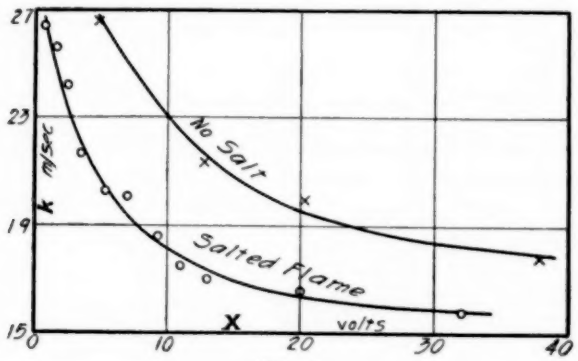

Fig. 1.

In conclusion I wish to thank Dr. H. A. Wilson for the suggestion of the problem and his kindly interest in the progress of the work, and particularly Dr. C. W. Heaps for his interest, invaluable criticisms and suggestions throughout the investigation and the writing of this paper.

THE RICE INSTITUTE,
HOUSTON, TEXAS,
August 18, 1924

THE OPTICAL CONSTANTS OF SOLID CAESIUM

By J. B. Nathanson

Abstract

The caesium mirror was prepared by filling a glass cell having two optical glass windows with liquid caesium distilled over in vacuum, the metal then being allowed to solidify. The index of refraction and the coefficient of absorption were determined by the polarimetric method. The caesium on glass mirror was placed in optical contact with the hypothenuse side of a right angle prism so that the light entered one leg and came out of the other. The absolute index of refraction was obtained from the observed value by multiplying the latter by the index of refraction of the glass, the coefficient of absorption remaining the same. The *index of refraction* was found to vary from 0.362 for λ4550A to 0.350 for λ6800A, with a minimum value of 0.321 for λ5890A. The *coefficient of absorption* increased from 2.37 for λ4550A to 4.34 for λ6800A. *The principal angles of incidence and of azimuth* calculated by means of Drude's formulas increased from 55°25′ and 38°32′ respectively for λ4550A to 63°20′ and 40°6′ for λ6800A. The corresponding values of the *reflecting power* were 44.2 and 66.1 per cent. The computed reflecting power of caesium in contact with crown glass increased from 48.5 per cent for λ4550A to 63.2 per cent for λ6800A. A direct spectro-photometric determination yielded corresponding values of 37.2 and 63.2 per cent, the agreement being best in the yellow and red end of the spectrum.

Introduction

DURING recent years, the alkali metals, by virtue of their interesting physical and chemical properties, have been the subject of many investigations. The optical constants are especially interesting, for they indicate an index of refraction less than unity and a very high reflecting power in the case of sodium and potassium. As early as 1898, Drude[1] determined the optical constants of molten sodium. Both sodium and potassium in the solid state were studied by R. W. and R. C. Duncan[2] using the polarimetric method that had been developed by Drude. The reflecting powers of sodium, potassium, and rubidium were studied by Nathanson[3] using a photo-electric cell as a photometer. The latter[4] also determined the optical properties of rubidium by the polarimetric method. Miss Frehafer[5] investigated the reflection and transmission of

[1] P. Drude, Ann. der Phys. **64,** 159 (1898)
[2] R. W. and R. C. Duncan, Phys. Rev. **36,** 294 (1913)
[3] J. B. Nathanson, Astrophys. J. **44,** 137 (1916)
[4] J. B. Nathanson, Phys. Rev. **11,** 227 (1918)
[5] Mabel K. Frehafer, Phys. Rev. **15,** 110 (1920)

ultraviolet light by sodium and potassium, using a photo-electric cell as a photometer. Quite recently the optical properties of sodium-potassium alloys were determined by Morgan[6] using the polarimetric method.

It was thought desirable to extend our knowledge of the optical properties of the alkali metals by studying caesium. Accordingly the optical constants of caesium were determined.

Preparation of the Caesium Mirror

The caesium mirror was formed by filling a small glass cell with the metal under vacuum. The insert *M* in Fig. 1, shows an enlarged end view of the cell. This cell consists of a Pyrex glass ring 1.8 cm internal diameter, to which is attached a connecting tube *L* of small bore. The edges of the ring were ground with emery and turpentine until the width

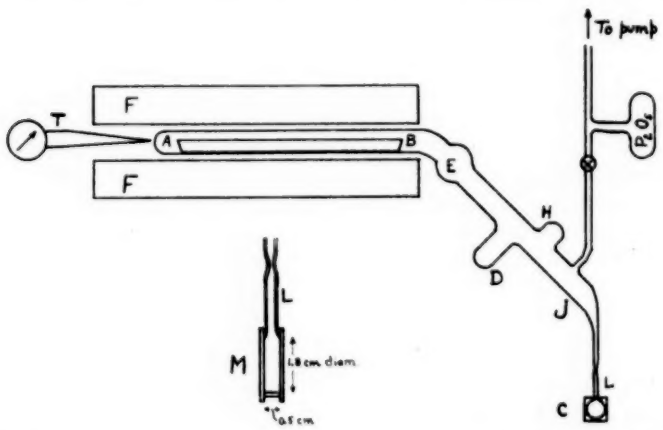

Fig. 1. Arrangement of apparatus for producing a caesium mirror.

of the ring approximated 0.5 cm, and then were polished with jeweler's rouge. After thorough cleansing a glass plate was cemented to each side of the ring by means of "Rock Cement," and the cell was baked for several hours in an electric oven kept at a temperature of about 110°C. It was found that with the cell so made, no difficulty was experienced in maintaining a high vacuum. The glass plates forming the windows of the cell were of high quality optical glass, 1.5 mm thick, and possessing a refractive index of 1.523 for sodium light. Each cell supplied two mirrors for investigation.

The glass cell *C* (Fig. 1) was connected by means of the tube *L* to the Pyrex glass apparatus in which the caesium was prepared. An intimate mixture of freshly prepared calcium filings and caesium chloride was

[6] R. Morgan, Phys. Rev. **20,** 203 (1922)

placed in an iron boat *B*, 30 cm long. This was then introduced into the horizontal tube and carefully sealed off at *A*. The boat and contents were heated by means of an electric furnace *F*, whose temperature was indicated by the thermo-couple *T*. The apparatus was evacuated by means of a Langmuir pump, the glass being thoroughly baked by applying bunsen flames to all parts.

The furnace was heated slowly to about 425° when first traces of caesium appeared in the condensing chamber *E*. The heating was continued, but the temperature was never allowed to rise above 625°C. The condensed caesium accumulated in the side tube *D*. When sufficient caesium had been collected, the tube *D* was placed in a small electric heater, and the caesium carefully redistilled at a temperature which never exceeded 200°C. By maintaining a burner between *E* and *D* during the redistillation, the caesium vapor was driven down to *J* and then condensed and collected in the cell *C*. The projection *H* acted as a condensing chamber. After the cell was filled with the molten caesium, it was detached by means of a blast lamp at the constriction in the tube *L*. The caesium remaining in the bottom of tube *J* was examined spectroscopically, and found to contain no traces of any impurities.

Some seven cells were filled with caesium, but the results are given only for the two cells whose mirrors seemed most perfect on inspection. The temperature of the laboratory did not exceed 23°C during the investigation, so that the caesium was always in the solid state.

Experimental Method and Formulas

The polarimetric method used in this investigation was essentially the same as that employed previously in the study of rubidium.[4] The apparatus at the disposal of the writer consisted of a large Geneva Society spectrometer, with the customary mounting of nicol prisms and simple Babinet compensator. The positions of the nicols could be read to 6′, while that of the Babinet compensator to about 5′. A 6.6 ampere single-filament gas-filled lamp furnished the light which was dispersed by means of a Hilger constant deviation spectrometer.

In order to avoid the disturbance produced by the glass surface of the mirror, the hypothenuse side of a right angle prism was placed in optical contact with the mirror by means of a little cedar oil, whose index of refraction was close to that of the glass. The light polarized in a plane at an angle of 45° with the plane of incidence, was incident normally on one leg of the prism (see Fig. 2), was reflected at an angle of 45° from the caesium-glass surface, and emerged normally from the other leg of the prism. The phase difference of the two components of the elliptically

polarized light and the azimuth of restored plane polarized light were determined by means of the compensator and analyzing nicol.

The glass cell C was held against the prism P by means of a sliding screw clamp S, Fig. 2, and the prism was held in place by brass strips BB. The latter were so attached to the prism table T that the reflecting surface was over the vertical axis of the spectrometer. This arrangement facilitated the removal and replacement of mirror and prism when observing the zero position of the compensator.

To attain as high an accuracy as possible, a large number of observations were made to determine the phase change and azimuth of the reflected light. The zero position of the compensator was determined for the four positions of the polarizer, ten individual settings being made for each of these four positions. This was repeated for the position of the compensator corresponding to a phase change of 360°. The mirror and

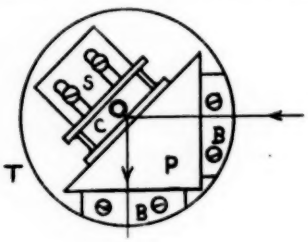

Fig. 2

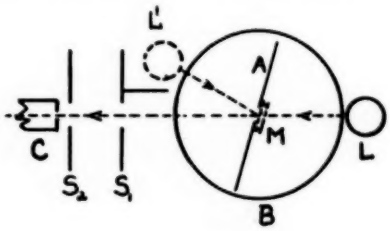

Fig. 3

Fig. 2. Mounting of prism and mirror on spectrometer table.
Fig. 3. Determination of the reflecting power of a caesium mirror by means of the Lummer-Brodhun spectrophotometer.

prism were then set in place, the telescope turned through 90° to receive the reflected light, and the new position of the compensator determined as before. Also for each of the polarizer positions, the positions of the analyzing nicol for total extinction of the light were carefully determined. From the means of all the sets of observations on the analyzing nicol, twice the angle of restored plane polarization was computed.

For the computation of the coefficient of absorption k and the index of refraction n, of the metal, Drude's formulas in the rigorous form were used, since the index of refraction is so low.

Let
$$\tan Q = \sin \Delta \tan 2\psi;$$
$$\cos 2P = \cos \Delta \sin 2\psi;$$
$$S = \sin 45^\circ \tan P;$$

where Δ is the phase difference and ψ the angle of azimuth. The coefficient of absorption k is then given by

$$k = \tan \tfrac{1}{2}X \qquad (1)$$

where $\tan X = S^2 \sin 2Q \,/\, (S^2 \cos 2Q + \sin^2 45°)$.

The index of refraction n was then evaluated by means of the equation

$$n^2 = (S^2 \cos 2Q + \sin^2 45°) \,/\, (1-k^2). \tag{2}$$

The reflecting power R for normal incidence is given by

$$R = \frac{n^2(1+k^2)-2n+1}{n^2(1+k^2)+2n+1}. \tag{3}$$

Results

The results for caesium in contact with crown glass are given in Table I. Only the data for the four best mirrors are listed.

Table I

Caesium in contact with crown glass

	Polarimetric method							Spectro-photo-metric	
λ	Mirror	Δ	2ψ	n	k	R	O	R
4550 A	No. 2	103° 29′	80° 2′	0.251	2.23	0.465	0.388	
	3	105 53	79 59	0.252	2.44	0.481	0.388	
	8	100 15	80 36	0.242	2.00	0.455	0.364	
	9	104 19	81 55	0.205	2.81	0.540	0.396	
	mean	103 29	80 38	0.238	2.37	0.485	0.384	0.372
4890	2	104 44	81 11	0.223	2.63	0.515	0.471	
	3	104 30	81 10	0.223	2.60	0.512	0.463	
	8	104 11	80 21	0.243	2.36	0.481	0.433	
	9	107 14	82 07	0.201	3.22	0.567	0.480	
	mean	105 10	81 12	0.223	2.70	0.519	0.462	0.457
5400	2	110 10	81 49	0.212	3.39	0.573	0.533	
	3	110 59	81 40	0.217	3.40	0.571	0.532	
	8	108 52	80 56	0.232	2.96	0.535	0.536	
	9	111 36	82 38	0.194	3.90	0.612	0.565	
	mean	110 24	81 46	0.214	3.41	0.573	0.542	0.541
5890	2	110 13	82 18	0.200	3.61	0.593	0.564	
	3	111 8	81 40	0.217	3.42	0.574	0.566	
	8	112 59	81 41	0.222	3.57	0.580	0.589	
	9	115 33	82 37	0.204	4.21	0.627	0.613	
	mean	112 28	82 4	0.211	3.70	0.594	0.583	0.586
6410	2	111 51	82 11	0.206	3.70	0.596	0.612	
	3	112 53	81 58	0.214	3.68	0.592	0.625	
	8	118 25	81 56	0.233	4.01	0.611	0.626	
	9	118 16	83 4	0.201	4.66	0.654	0.637	
	mean	115 21	82 17	0.214	4.01	0.613	0.625	0.629
6800	2	116 1	82 22	0.212	4.10	0.619	0.618	
	3	121 55	81 54	0.251	4.12	0.617	0.620	
	8	122 11	82 11	0.245	4.28	0.630	0.630	
	9	121 26	83 6	0.213	4.84	0.663	0.638	
	mean	120 23	82 23	0.230	4.34	0.632	0.627	0.632

The mean results for n and k are plotted in Fig. 4. The index of refraction seems to be a minimum in the visible spectrum for a wave-length of 5890 A. The coefficient increases steadily from a value of 2.37 for λ4550 A to a value of 4.34 for λ6800 A.

The values for the computed reflecting power R are listed in column seven of Table I. It was thought desirable to compare these computed results with the values obtained more directly by means of a Lummer-Brodhun spectrophotometer.

The arrangement of apparatus is shown in Fig. 3. An ordinary spectrometer B was placed in front of the collimator C of the spectrophotometer. The telescope was removed, and in its place was mounted a white light bulb L. In place of the spectrometer prism table was mounted a screen A painted a dull black color and containing a circular aperture slightly smaller in diameter than the caesium mirror. By means of small clamps, the mirror was mounted right behind the circular aperture and over the center of the spectrometer. Screens S_1 and S_2 served to prevent stray light from reaching the collimator of the spectrophotometer.

The procedure in observation was as follows. With the mirror removed and the light at L ten settings were made with the spectrophotometer. The mirror was then mounted at M, the light turned through an angle of 180° minus twice the angle of incidence, to position L'. Observations were then made on the reflected light. The reflecting power of the caesium glass mirror is given by the ratio of the sector readings after and before reflection.

In order to compute the reflecting power of caesium in contact with glass, allowance must be made for reflection at the front face of the glass, multiple internal reflection, and absorption in the glass itself. A formula to correct for these disturbances had been previously[3] developed in the study of the reflecting powers of the alkali metals.

Let O = the observed reflecting power of the mirror (metal plus glass);
r = reflecting power of the front glass surface (air to glass to air);
r' = reflecting power of glass surface (glass to air to glass)
t = transmission power of the glass plate per single passage of the light.
The reflecting power R of the caesium in contact with glass is given by

$$R = (O-r) \;/\; [t^2(1+Or'-r-r')]. \qquad (4)$$

The angle of incidence of the light on the front face of the glass surface was kept at 20° throughout the investigation with the spectrophotometer. From previous data,[3] r was taken as 0.042, r' as 0.035, The transmission t was redetermined and found to be 0.99. The variation of these quantities with wave-length is quite negligible. The actual angle of incidence

of the light on the caesium was about 13°. A test showed that there is very little variation in the reflecting power with the angle of incidence up to 30°, so that the reflecting power of caesium as computed may be taken as the value that would have been obtained for normal incidence. The values of O are given in the eighth column of Table I, while the values of R as computed by Eq. (4) are shown in the last column of the same table. For purposes of comparison, the values of the reflecting power of caesium in contact with glass, as obtained by the polarimetric and spectrophotometric methods are plotted in Fig. 5. It will be noted that the agreement is quite satisfactory for wave-lengths greater than 5500 A but is not so good for smaller wave-lengths, the deviation becoming more marked the smaller the wave-length. It is true that the observational difficulties are the greatest for the violet end of the spectrum,

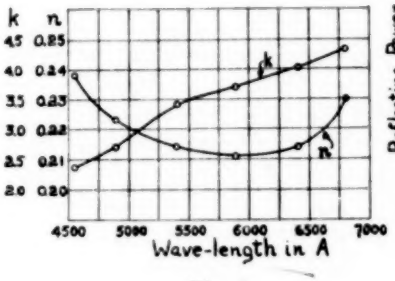

Fig. 4

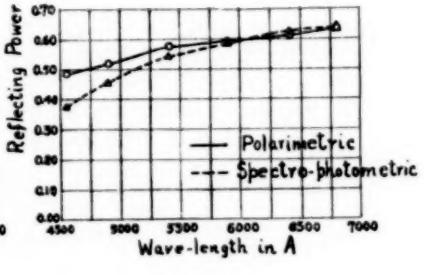

Fig. 5

Fig. 4. Coefficient of absorption k and index of refraction n of caesium in contact with glass.

Fig. 5. Reflecting power of caesium in contact with glass.

but the deviation in the reflecting powers as obtained by the two methods appears in the green part of the spectrum for which the eye is most sensitive. Conroy[7] found that the direct method yielded values for white light which were several per cent less than the values obtained by the polarimetric method for sodium light. Tate's work[8] with a glass-silver surface indicates a somewhat similar experience to the one with caesium, though the deviation in the results obtained by Tate were not quite so marked. If there is any discrepancy in the reflecting power as obtained by the two methods, the deviation should become most marked in the ultra-violet.

It is of course desirable to know what the optical constants of caesium would be with respect to air. The customary procedure has been to

[7] Sir J. C. Conroy, Proc. Roy. Soc. **36,** 196 (1884)

[8] J. T. Tate, Phys. Rev. **34,** 326 (1912)

assume that the coefficient of absorption remains unaffected by the transparent medium in contact with the metal, but that the index of refraction of the metal with respect to air can be obtained from the index with respect to the medium, by multiplying the latter by the index of refraction of the transparent medium. This procedure has been verified experimentally by a number of investigators.[9] Further verification has also been made by the writer who determined the optical constants of silver when in contact with air and glass, the method of investigation being the same as that employed in the study of caesium.

These conclusions have been applied to caesium, the constants with respect to air being computed from the mean results given in Table I. The computed values are shown in Table III. The values of k are listed again for convenience. The principle angles of incidence $\bar{\phi}$ and of azimuth $\bar{\psi}$, are given in columns 5 and 6 respectively. The values of ϕ were evaluated graphically by means of Eq. (5)

$$\sin^4 \bar{\phi} \tan^4 \bar{\phi} = n^4(k^2+1)^2 + 2n^2(k^2-1) \sin^2 \bar{\phi} + \sin^4 \phi. \quad (5)$$

The angle $\bar{\psi}$ was then similarly evaluated from Eq. (6)

$$\tan^2 \bar{\phi} \cos 4\bar{\psi} + 1 = (\tan^2 \phi \,/\, \tan X) \sin 4\bar{\psi}. \quad (6)$$

TABLE III

Optical constants of caesium with reference to air

λ	n	k	R(calc.)	$\bar{\phi}$	$\bar{\psi}$
4550 A	0.362	2.37	0.442	55° 25′	38° 32′
4890	0.339	2.70	0.485	56 13	39 6
5400	0.326	3.41	0.565	58 48	39 43
5890	0.321	3.70	0.594	59 44	39 54
6410	0.326	4.01	0.625	61 8	40 3
6800	0.350	4.34	0.661	63 20	40 6

The reflecting power R is given in the fourth column. The reflection appears to be selective, as the reflecting power for the red end of the spectrum is about fifty per cent greater than that for the violet end. The minimum value of the refractive index obtained for λ5890 A seems to be in accordance with the experience of the Duncans[2] for the element sodium. Their dispersion curve for sodium showed a sharp minimum for λ5893. The values of the refractive index for caesium do not change so abruptly.

[9] W. Voigt, Wied. Ann. **23,** 134 (1884);
P. Drude, Wied. Ann. **39,** 481 (1890);
L. R. Ingersoll and R. T. Birge, Phys. Rev. **29,** 392 (1909);
L. P. Wheeler, Phil. Mag. **22,** 229 (1911).

In order to correlate the optical absorption of the various alkali metals, the values of the coefficients of absorption have been plotted in Fig. 6. The data for the three wave-lengths has been obtained from the work of the Duncans[2] on sodium and potassium, and from the writer's results on rubidium[4] and caesium. It is very interesting to note the regularity with which absorption coefficients diminish with atomic number, the values varying inversely as about the three halves or second power of the atomic number. On the other hand the refractive index is found to increase with the atomic number.

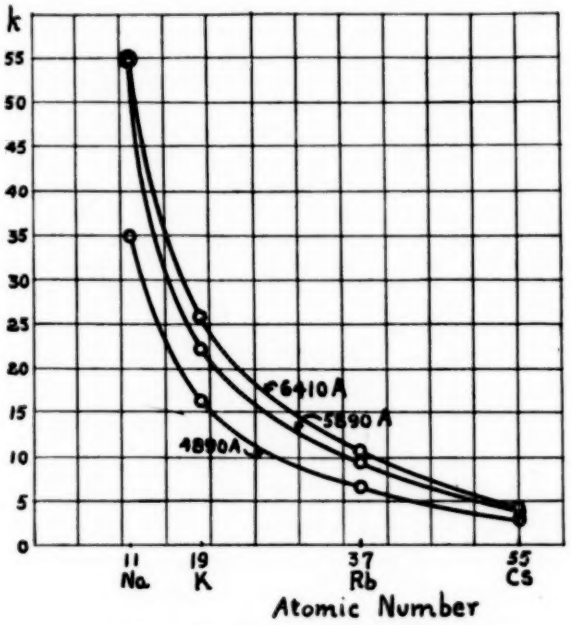

Fig. 6. Variation with atomic number of the coefficients of absorption of the alkali metals.

A computation of the number of free electrons per atom according to Drude's[10] electron theory of metallic dispersion, yields values ranging from 1.5 for λ6800 A to 2.3 for λ4550 A. As would be expected there is a very large discrepancy between the specific resistance of caesium as determined by electrical methods and as computed from the optical constants, the optical method giving values six to seven times that obtained by electrical methods. Obviously then, until the mechanism of electrical conduction is understood more fully, little can be gained by such computations.

[10] P. Drude, Ann. der Phys. **14**, 936 (1904)

It is intended to continue this investigation on caesium in the liquid state so that we might have more experimental information on the relation between optical and electrical properties.

I take this opportunity of expressing my thanks to the Committee on Research of the Carnegie Institute of Technology for funds granted to me for carrying out of this investigation.

CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PA.
July 31, 1924

A UNIVERSAL CALIBRATION CURVE FOR BALLISTIC GALVANOMETERS

By D. P. Randall

Abstract

Universal curve for determining sensitivity of ballistic galvanometers under all conditions of circuit resistance.—On closed circuit, the throws produced by a given discharge depend on the circuit resistance because of its effect on the damping. No simple relation between sensitivity and circuit resistance is known which is applicable to a wide range of instruments and damping. However if sensitivity is expressed as a fraction of undamped sensitivity, and circuit resistance as a fraction of critical damping resistance, a general mathematical relation between these two quantities is obtained which is true for all moving-coil type instruments. Numerical data are given and also the curve. A special damping coil may be treated as an equivalent parallel circuit, and the joint effect determined accordingly. The accuracy is limited only by the precision of measurement of undamped sensitivity and critical damping resistance, as no approximations are involved in the derivation.

WHEN a moving-coil ballistic galvanometer is used in a closed circuit, its sensitivity is diminished because of the electromagnetic damping produced by the current induced in the moving coil. The change in sensitivity depends on the circuit resistance, but not in any readily calculable manner. When the damping is slight, the proper correction can be quite simply determined from the observed decrement; but the approximation involved becomes progressively worse as the damping is increased, so that the method loses its validity altogether for decrements greater than about 1.2.

Various attempts have been made to establish a relation, more or less empirical, between the change in sensitivity and the circuit resistance.[1] The use of the methods proposed involves all the errors incident to extensive interpolations, and further requires that the galvanometer be practically undamped on open circuit. In other words, they are useless for an instrument with considerable auxiliary damping. It is the purpose of the present article to show that a universal calibration curve is possible for all instruments of the moving-coil type, and that from this curve the sensitivity corresponding to any desired circuit resistance may readily be determined.

The general proposition (the truth of which will appear later) upon which the derivation of the desired relation is based, is that the calibra-

[1] See e. g. Morton Masius, Phys. Rev. **23**, 649 (1924)

tion curves of all galvanometers reduce to a single curve when expressed in terms of undamped sensitivity K_0 and critical damping resistance R_c. Both of these quantities are readily measurable. From them and the "universal curve," the sensitivity corresponding to any given circuit resistance is determined by a simple proportion.

For example, suppose a galvanometer of undamped sensitivity 120 mm/μ-coulomb and critical damping resistance 300 ohms, is to be used in a circuit of 450 ohms resistance. The ratio of circuit resistance to critical damping resistance, n, is 1.5. K/K_0, the corresponding ratio of ballistic sensitivity to undamped sensitivity, is found from the curve, Fig. 1, to be .471. Hence the desired sensitivity is

$$K = .471 \times 120 = 56.5 \text{ mm}/\mu\text{-coulomb}.$$

The same result is of course obtained whatever the units in which K and K_0 are expressed.

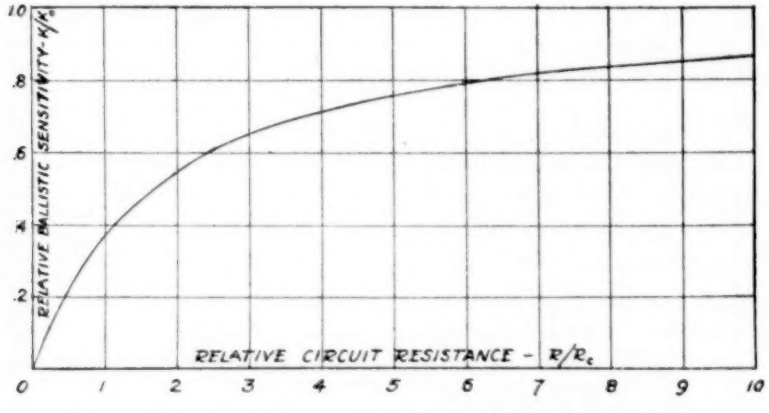

Fig. 1. Universal calibration curve for ballistic galvanometers.

If an auxiliary damping coil or other damping device is employed, the method is a little more elaborate. The value of the *equivalent circuit resistance* n' of the auxiliary device (expressed as a fraction of R_c) must be found (see Eq. 10), and the value of n appropriate to the actual circuit be combined with it as a *parallel resistance*. For example, suppose in the case illustrated above, an auxiliary coil gave a decrement of 1.7 to the instrument on open circuit. Then λ the logarithmic decrement per half cycle is .531, and n' (Eq. 10) is 6.00. The parallel resistance of n and n' is $1.5 \times 6.0/7.5 = 1.2$. The corresponding ratio K/K_0 (from the curve) is .414. Hence the desired sensitivity is

$$K = .414 \times 120 = 49.7 \text{ mm}/\mu\text{-coulomb}.$$

An outline of the theory is as follows. The solution of the general equation of motion of the moving-coil galvanometer[2]

$$P\,d^2\theta/dt^2 + k\,d\theta/dt + \tau\,\theta = \beta\,i$$

leads, in the case of "instantaneous discharge," to the following three expressions for sensitivity:

$$K=\theta/Q=(2\pi C/T_0)\epsilon^{-a t_1} \tag{1}$$

$$K=\theta/Q=(2\pi C/T_0)\epsilon^{-1} \tag{2}$$

$$K=\theta/Q=(2\pi C/T_0)(2\pi/T_0)\epsilon^{m_1 t_1}/m_2 \tag{3}$$

corresponding to the oscillatory, critically damped, and over-damped conditions respectively. In these equations C is the current sensitivity of the instrument, T_0 its undamped period, and t_1 the time required for the first throw (determined from the condition that $d\theta/dt=0$); while a, b, etc., are given by $a=k/2P$; $b=\sqrt{\tau/P-a^2}$; $m_1=-a+jb$; $m_2=-a-jb$; $t_1=(1/b)\tan^{-1}(b/a)$ or $[1/(m_1-m_2)]\log(m_2/m_1)$. Expressed as a fraction of the undamped sensitivity K_0 ($K_0=2\pi C/T_0$) Eqs. (1) to (3) become

$$K/K_0=\epsilon^{-a t_1} \tag{4}$$

$$K/K_0=\epsilon^{-1} \tag{5}$$

$$K/K_0=(2\pi/T_0)\epsilon^{m_1 t_1}/m_2\,. \tag{6}$$

If the damping is entirely electromagnetic, the damping coefficient k is inversely proportional to the circuit resistance R, or $k=k_0/R$. Expressing R as a fraction of the critical damping resistance, $R=nR_c$, and $k=k_0/nR_c=k_c/n$, where k_c is the critical value of the damping coefficient. Consequently

$$a=(1/n)\,(k_c/2P)=(1/n)\sqrt{\tau/P}$$
$$b=(1/n)\sqrt{(\tau/P)\,(n^2-1)}$$

and Eqs. (4) to (6) reduce to

$$K/K_0=\epsilon^{-\left[1/\sqrt{n^2-1}\right]\tan^{-1}\sqrt{n^2-1}} \tag{7}$$

$$K/K_0=\epsilon^{-1} \tag{8}$$

$$K/K_0=\left[n/(1+\sqrt{1-n^2})\right]\epsilon^{-\frac{1-\sqrt{1-n^2}}{2\sqrt{1-n^2}}\log\frac{1+\sqrt{1-n^2}}{1-\sqrt{1-n^2}}} \tag{9}$$

In these equations the individuality of the galvanometer has entirely disappeared. Relative sensitivity K/K_0, relative circuit resistance R/R_c ($=n$), are all that remain. Consequently a graphical expression of the functional relationship between K/K_0 and R/R_c constitutes a

[2] See e. g. Laws, Electrical Measurements, p. 109 ff.

"universal calibration curve" that is applicable to all ballistic galvanometers of the moving-coil type. Such a curve is shown in Fig. 1. The data from which this curve was plotted are given in the table below.

R/R_c	K/K_0	R/R_c	K/K_0
0.100	.0494	2.000	.5463
0.200	.0964	2.500	.6029
0.300	.1403	3.000	.6471
0.400	.1810	3.500	.6825
0.500	.2186	4.000	.7115
0.600	.2533	5.000	.7561
0.700	.2853	6.000	.7888
0.800	.3150	8.000	.8335
0.900	.3424	10.000	.8626
1.000	.3679	20.000	.9267
1.500	.4713	50.000	.9695

If auxiliary damping is present, $k=k'+k_0/R=k_0/R'+k_0/R=k_0(1/R'+1/R)$, where k' or k_0/R' represents the damping coefficient of the instrument on open circuit. The form of the last equation suggests at once the relation of parallel resistances; so that we have only to treat the auxiliary damping device as an equivalent parallel circuit, and determine its apparent resistance as shown above, in order to take account of it completely in making use of the "universal calibration curve."

The relation between n' and the logarithmic decrement per half cycle λ is readily derived thus: $\lambda=aT/2=\pi a/b=\pi/\sqrt{n^2-1}$.

Hence
$$n'=\sqrt{\pi^2/\lambda^2+1}. \tag{10}$$

From this equation the "equivalent circuit resistance" n' of the auxiliary damping may be found by measuring the corresponding decrement.

Another method of determining "equivalent circuit resistance" which may give greater precision when λ is large, requires the measurement of the critical damping resistance R_c'' with the auxiliary damping device applied. For the true critical damping resistance R_c (electromagnetic damping only) should evidently represent the joint effect of the actual circuit resistance R_c'' and the "equivalent circuit resistance" R' of the auxiliary damping, considered as parallel resistances. Thus $R_c=R_c''R'/(R_c''+R')$, or

$$n'=n''/(n''-1). \tag{11}$$

Several Leeds and Northrup galvanometers, both with and without auxiliary damping coils, were calibrated by the condenser discharge method on open circuit and by the standard mutual inductance method with various degrees of electromagnetic damping. In each case the sensitivity thus determined agreed within experimental error with that

determined from the "universal calibration curve." Similarly values of n' for each of the galvanometers, determined by both of the above methods, were found to agree with each other within the same limits. As there are no approximations involved in the above derivations, the only limit to the accuracy of the method would seem to be set by the possible precision of measurement of K_0 and R_c, the respective undamped sensitivity and critical damping resistance.

SYRACUSE UNIVERSITY,
June 13, 1924

ACOUSTIC WAVE FILTERS; AN EXTENSION OF THE THEORY

By G. W. Stewart

Abstract

Extension of theory of acoustic wave filters to high frequencies.—In the simple form of acoustic wave filter theory already published, the wave-length was assumed long in comparison with the length of a section of the conduit. Experimentally additional bands appeared at higher frequencies and these are now discussed. Advantage is taken of the recurrence at higher frequencies of the vanishing of the acoustic impedance of a section of the conduit, and approximate values of the components of this impedance are established for the neighboring region of frequencies. *Formulas for low-pass and single-band-pass filters*, using these values, are found to give the experimental cutoffs of the additional bands with satisfactory accuracy. By appropriate design an additional band can be made practically to disappear. Tables showing agreement of experiment with theory are given. The theory is thus extended to higher frequencies but not to those for which additional resonance frequencies of the branches occur.

IN a discussion[1] of an approximate theory of acoustic wave filters for low-frequency-pass, high-frequency-pass and single-band-pass acoustic wave filters, it became evident that correct expressions for the acoustic impedances in the transmitting conduit and in its branches could not readily be obtained, and attention was confined to the securing of approximate formulas. The theory based on these approximations can be relied upon only if the wave-length is larger than several times the length of a section in the transmitting conduit.

Eqs. (5) and (6) of the preceding paper state that there is transmission through such a filter only between the frequencies represented by the following values of the ratios of the acoustic impedance in a section of the transmission line and in a branch: $Z_1/Z_2=0$ and $Z_1/Z_2=-4$. Transmission occurs at all frequencies at which Z_1 and Z_2 are of opposite signs and the absolute value of Z_1 is not greater than four times that of Z_2. It is not difficult to see that there will be transmission at frequencies other than the ranges specified by the values of Z_1 and Z_2 used in the simple theory.[1] For in every case considered Z_1 and Z_2 were composed of inertances and capacitances in series and in parallel or in a combination of these. Zobel[2] has shown that if there are two reactances which increase

[1] Stewart, Phys. Rev. **20**, 528 (1922)

[2] Zobel, Bell System Technical Journal **2**, 1 (Jan. 1923)

with frequency, their series and parallel combinations will also increase with frequency. His discussion concerns electrical reactances but is readily seen to be applicable to the acoustic case. In the acoustic filters the impedances were[1] combinations of the reactances, $iM\omega$ and $-i/C\omega$, ω being 2π times the frequency, M the inertance and C the capacitance. The change of these reactances with frequency is positive and hence, according to the above theorem, the changes of Z_1 and of Z_2 with frequency are positive. Since there is a band of transmission from the frequency where $Z_1=0$ to the frequency where $Z_1=-4Z_2$, one may expect that in the acoustic filters there will be a transmission band with one frequency limit wherever $Z_1=0$, and this value will occur at the resonance frequency of a section of the transmitting conduit. Since in all the acoustic filters thus far constructed a simple tubular conduit is used for the transmission line, the resonance frequencies are practically harmonic; also the frequencies for which $Z_1=0$ can be predicted, and, as will be shown, this leads to the location of additional transmission bands not indicated by the earlier approximate theory.[1] This procedure is possible, however, only in case the expression for Z_2 is known. Now it happens that the filters enumerated in this article have branches such that the formulas for Z_2 are approximately correct over the entire range of frequencies considered, and consequently the above method of locating the bands is applicable.

Low-frequency-pass Filters

The formulas for low-frequency-pass filters found most acceptable in the previous report were $f_1=0$, and $f_2=(1/\pi)\ (M_1C_2+4M_2C_2)^{-1/2}$, wherein f_1 and f_2 are the limiting frequencies of a band of zero attenuation, M and C are respectively the inertance and capacitance, and the subscripts of the last two refer respectively to the conduit and branch as indicated by Z_1 and Z_2. In obtaining these equations it was assumed that C_1 was zero. The justification was chiefly that the length of a section of the conduit was very short compared to a wave-length and the fluid could be assumed as moving as a whole. There seems to be no simple escape from the policy of assuming approximate values of Z_1, and the present discussion really concerns a method of approximating the values of the reactance components of Z_1 in higher frequency regions near where $Z_1=0$, (i.e. near the resonance frequencies of each section of the conduit) so that predicted values of the recurring bands may be obtained. If Z_1 is a tube of length l_1, open at both ends, we have the resonance frequencies $na/2l_1$ where n is an integer. We know that in the actual case there will be such resonance frequencies if the sizes of the openings are sufficient. Such a tube in the

resonance frequency region may be regarded as approximately equivalent to an inertance M_1 and a capacitance C_1 in series, or $Z_1 = i(M_1\omega - 1/C_1\omega)$. In the simpler theory[1] Z_1 was merely $iM_1\omega$. The value of Z_2 is, however, carried over into this extension of the theory without change because it is sufficiently exact. Its value is $i(M_2\omega - 1/C_2\omega)$. The procedure involves the adoption of these values of Z_1 and Z_2, substituting them in the standard equations for the attenuation limits, $Z_1/Z_2 = 0$ and $Z_1/Z_2 = -4$. There is then obtained the following:

$$2\pi f_1 = (M_1C_1)^{-1/2};\ 2\pi f_2 = [(1/C_1 + 4/C_2)/(M_1 + 4M_2)]^{1/2}. \qquad (1)$$

These equations occur in the previous article[1] but were not applicable to the filters at low frequencies. Here they will be accepted under the condition that they apply only in the frequency region of resonance $[Z_1 = 0]$. The equivalent M_1 and C_1 are not separately determined by the vanishing of Z_1, but by an additional consideration to be mentioned. Knowing the equivalent inertance and capacitance, M_1 and C_1, the attenuation limits can be obtained from Eq. (1). The essence of the method is the knowledge of the values of the *equivalent* M_1 and C_1 in each frequency region where $Z_1 = 0$. The method assumes no change in the form of Z_2 or in the values of M_2 and C_2.

Single-band Filters

Adopting the above form of Z_1 and the value of

$$Z_2 = iM_2\omega(M_2'C_2\omega^2 - 1)/(M_2C_2\omega^2 + M_2'C_2\omega^2 - 1)$$

as previously[1] used for a single band filter we get the following values of attenuation limits,

$$2\pi f_1 = (M_1C_1)^{-1/2},\ 2\pi f_2 = [(M_2C_2(1 + M_2'/M_2)\ )]^{-1/2}$$
$$2\pi f_3 \text{ or } 2\pi f_4 = (M_2C_2)^{-1/2}[A \pm (A^2 - B)^{1/2}]^{1/2}$$

wherein

$$A = \tfrac{1}{2}C_1^{-1}(M_1C_1 + M_2C_2 + M_2'C_2 + 4M_2C_1)(M_1 + M_1M_2'/M_2 + 4M_2')^{-1}$$
$$B = M_2C_2C_1^{-1}(M_1 + M_1M_2'/M_2 + 4M_2')^{-1}.$$

In accord with what has been stated, the new approximate expressions later to be obtained for M_1 and C_1 are to be accepted only in the neighborhood of the frequency f_1 corresponding to $Z_1 = 0$. Hence if the computed values of f_3 or f_4 prove to be far removed from this frequency region, they should receive no consideration. In the cases of filters here recorded, f_4 falls in a region of much lower frequency where the old approximation for Z_1 holds and hence f_4 cannot be considered, while f_2 is the same form as in the earlier theory and is one of the cutoffs of the first band, formerly

described as a single band. Hence in the additional bands f_1 and f_3, only, will be considered In the case of a more complicated filter a variable single band pass filter,[3] Z_2 has the more complicated expression,

$$Z_2 = i[M_2''\omega(M_2C_2\omega^2 + M_2'C_2\omega^2 - 1) + M_2\omega(M_2'C_2\omega^2 - 1)](M_2C_2\omega^2 + M_2'C_2\omega^2 - 1)^{-1}.$$

Here M_2'' is the inertance of the orifice introduced in series with the side branch. When this new value of Z_2 is used, the equations for f_1 and f_3 are as follows:

$$2\pi f_1 = (M_1C_1)^{-1/2};\ 2\pi f_3 = [A + (A^2 - B)^{1/2}]^{1/2} \tag{3}$$

where $B^{-1} = C_1C_2[M_1M_2 + M_1M_2' + 4M_2''\ (M_2 + M_2') + 4M_2M_2']$; (3)

$$A = \tfrac{1}{2}B[M_2C_2 + M_2'C_2 + C_1\ (4M_2'' + 4M_2 + M_1)\ ].$$

Application of Equations

If the values of M_1 and C_1 were known, the equations (1) and f_1 and f_3 of equations (2) and (3) could be at once applied, the former to low-pass and the latter to single-band-pass filters. In the earlier work[1] the value of M_1 for a section of a conduit was $\rho l_1/S_1$, wherein l_1 was the length and S_1 the area of the conduit and ρ was the density of the gas. Also C_1 was $V_1/\rho a^2$, where V_1 was the volume considered and a was the velocity of sound. If these two expressions are applied to a section of a conduit, the product is $M_1C_1 = l_1^2/a^2$, but this cannot be correct in the region $Z_1 = 0$, for here, as shown by the formula for Z_1, $M_1C_1 = 1/\omega^2$ and, from elementary acoustics, at resonance $1/\omega = l_1/n\pi a$. Consequently it will here be assumed that the *equivalent* M_1 and C_1 are such that $(M_1C_1)^{1/2} = l_1/n\pi a$. Obviously this product will occur if, instead of the earlier expressions for M_1 and C_1 the following somewhat empirical values be used: $M_1 = \rho_1 l_1/S_1\alpha$ and $C_1 = V_1/\rho a^2\beta$, wherein $\alpha\beta = n^2\pi^2$. By trial it was shown that a fairly satisfactory confirmation of the equations could be obtained if the following values of α and β were adopted. For low-pass filters, $\alpha = 1$, $\beta = n^2\pi^2$; for single-band-pass filters, $\alpha = n$ and $\beta = n\pi$. The reason no attention in this connection is given to high pass filters is that throughout the attenuation region the assumption of relatively long wave-length is sufficiently accurate, and transmission seems to be excellent at higher frequencies. There are, however, effects in this transmission region which may be discussed at a later time.

The values of the other symbols in our equations are as follows: $M_2 = \rho/c$ with low-pass; $M_2 = \rho l_2/S_2$ with single-band-pass filters, wherein

[3] Stewart, Phys. Rev. **22**, 502 (1923)

c is the conductivity of the orifice into the volume in the side branch; $M_2' = \rho/c'$, wherein c' is the conductivity of the orifice into the side branch and $C_2 = V_2/\rho a^2$. These, together with $M_1 = \rho l_1/S_1\alpha$ and $C_1 = V_1/(\rho a^2\beta)$ are substituted in Eqs. (1), (2) and (3) as indicated, and the additional bands are found, one for each value of n. Attention should be called to the fact that it is possible to cause one and sometimes more of the additional transmission bands to disappear by using in series filters

TABLE I

No.	No. sects.	l_1 (cm)	r_1 (cm)	V_2 (cm³)	f_∞ (obs.)	f_1'* (calc.)	f_{11} (obs.)	f_{11} (calc.)
H−2	3	2.66	.243	21.6	450	524	5300	4820
H−3	5	5.0	.243	43.1	230	291	3200	3115
H13−5	5	4.0	1.42	44.4	920	1360	3400	3125
$H13_1$−10C†	10	4.0	1.42	44.4	1000	1118	3675	3520
$H13_2$−10C	10	4.0	1.42	44.4	660	952	3100	3040
H13− 5C	5	8.0	1.42	44.4	825	875		2060
H13− 3C	3	12.0	1.42	44.4	700	750	1500	1433
H13− 2C	2	16.0	1.42	44.4	670	664	1110	910
H−15−16	4	1.67	.75	5.94	2200	2710	6400	6660
H−15− 8	4	1.67	.75	5.94	1700	2120	5600	4580
H−16−16	4	1.67	.75	2.62	3200	4085	7200	7030
H−16− 8	4	1.67	.75	2.62	2500	3200	5800	5700
H−17−16	4	1.67	.75	4.36	2700	3175	6400	6870
H−17− 8	4	1.67	.75	4.36	2200	2480	5500	4720
H−18	2	1.00	.401	1.59	2800	3265		9600
R−1	3	1.58	1.19	7.1	2700	2840	5050	5370
R−2	4	1.58	1.19	7.1	2750	2840	5200	5370
R−3	4	1.32	1.19	5.87	3350	3170	5750	5910
R−4	4	1.45	1.19	6.48	3025	3010	6400	5350
R−5	6	2.58	1.19	11.82	2000	2095	3800	3940
R−6	6	1.58	1.19	7.1	2075	2100	3900	3930
R−6	6	1.58	1.19	7.1	2700	2700	5300	5040

No.	f_{12} (obs.)	f_{12} (calc.)	f_{21} (obs.)	f_{21} (calc.)	f_{22} (obs.)	f_{22} (calc.)	f_{31} (obs.)	f_{31} (calc.)
H−2	6500	6460				12920		
H−3	3400	3440	6200	6250	6800	6880		
$H13_1$−10C	3900	4300	7600	6970		8600		
$H13_2$−10C	4500	4300	6300	5710	7700	8600		
H13− 5C		2150	4300	3720	4700	4300	5900	5570
H13− 3C	1650	1528		2820		2866		4080
H13− 2C	1300	1074	1900	2100	2000	2150	2900	3070

No.	f_{32} (obs.)	f_{32} (calc.)	f_{41} (obs.)	f_{41} (calc.)	f_{42} (obs.)	f_{42} (calc.)	f_{51} (obs.)	f_{51} (calc.)	f_{52} (obs.)	f_{52} (calc.)
H13−5C	6800	6450		8600						
H13−3C		4300		5400		5733	6800	6750	7400	7160
H13−2C	3200	3225	4000	4040	4070	4300	5300	5000	5800	5370

* All calculated values were obtained by use of Eq. (1) except f_1' (calc.) for which the original equations were used.

† The additional designation, C indicates the presence of a core in the series section, thus changing the area.

possessing the same transmission region at low frequencies and yet differently located transmission bands at high frequencies. This is possible since the additional bands depend only on the conduit dimensions, if branches are used for which the Z_2's can be expressed with fair accuracy throughout the entire range. It is also possible to determine the dimensions that will cause the limits of an additional band to coalesce and thus remove the band.

TABLE II

No.	No. Sects.	l_1 (cm)	r_1 (cm)	V_2 (cm³)	c	F_1 (obs.)	F_1 (calc.)	F_2 (obs.)	F_2 (calc.)
1	3	5.0	.243	42.7	.69	190	224	260	346
2	3	3.66	.243	21.19	.69	275	318	375	575
3	3	5.0	.243	28.02	.69	270	283	370	430
4	3	2.66	.243	14.81	.69	430	436	520	707
5	3	5.00	.243	28.02	.69	190	234	270	410
6	3	2.66	.243	14.81	.69	350	349	500	680
9	3	2.66	.243	22.7	.420	285	275	455	499
9_1	3	2.66	.243	22.7	.420	285	275	350	387
9_2	3	2.66	.243	22.7	.420	285	275	390	439
10	4	1.77	1.12	6.11	.556	775	850	1150	1180
20_1	5	2	1.42	20.4	1.67	670	673	1075	1390
20_2	5	2	1.42	20.68	2.3	680	684	1200	1555
20_3	5	2	1.42	20.0	2.25	860	885	1550	1638
20_4	5	2	1.42	20.66	3.18	890	910	1560	1770

No.	f_{11} (obs.)	$f_{11}(2)$ (calc.)†	f_{12} (obs.)	$f_{12}(2)$ (calc.)	f_{21} (obs.)	$f_{21}(2)$ (calc.)	f_{22} (obs.)	$f_{22}(2)$ (calc.)
1	2300	2125	3740	3440	5000	4210	7700	6880
2	3400	3720	6200	6450				
3	2500	2725	3600	3440	5450	4620	7000	6880
4	3300	4500	6600	6450				
5	2675	2730	3475	3440	5900	5410	7600	6880
6	3500	4440	6150	6450				
9	4300	3470	6300	6450				
9_1	2700	*1935	5500	*6450				
9_2	4100	*2460	6200	*6450				
10	3900	3400		9730				
20_1	3000	2995	6800	8600				
20_2	2975	3775	6800	8600				
20_3	3650	3500	6200	8600				
20_4	3600	3972	6800	8600				

* Computed from Eq. (3).

EXPERIMENTAL RESULTS

Following a method already described,[1] transmission measurements were made of a number of filters. The data concerning them including their dimensions and cut-off frequencies are presented in the accompanying tables. In Table I are the data for the low-pass filters having the experimental cut-off's $f_\infty, f_{11}, f_{12}, f_{21}, f_{22}$, etc. The corresponding calculated

frequencies were computed according to equation (1) excepting f_1' which was made according to the original equations. The subscripts 11 and 12 indicate the limits of the first band, 21 and 22 of the second, etc. In Table II are recorded the data for the single-band-pass filters. Here F_1 and F_2 are the cut-offs of each of the "single bands" experimentally determined and F_1(calc.) and F_2 (calc.) are the corresponding cut-offs as determined by the original equations. Some of these values, as likewise some of the f_1' values in Table I, have already been published.[1] The columns f_{11} and f_{12} are the experimental values, and f_{11} (2) and f_{12} (2) are the values computed according to equation (2). In the cases of 9_1 and

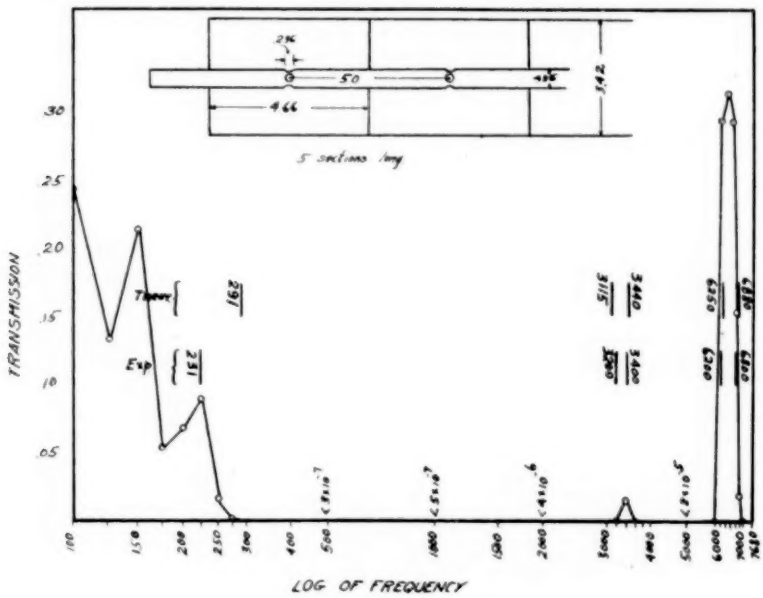

Fig. 1. A large attenuation range and two additional bands in a low-pass filter.

9_2 filters Eq. (3) is used instead of Eq. (2). A blank in a table indicates that the measurement or computation was above the range of frequencies used, or that the filter was no longer available for measurements, or that the transmission was too small to permit the location of the band. Throughout both tables there is a fairly satisfactory agreement of computation with experiment.

Fig. 1 shows a low frequency pass filter the dimensions of which are such that the additional bands do not appear until the frequency has reached ten times the cut-off frequency. In Fig. 2 the first additional band is nearer. In Fig. 3 is the case of a single band filter. These three

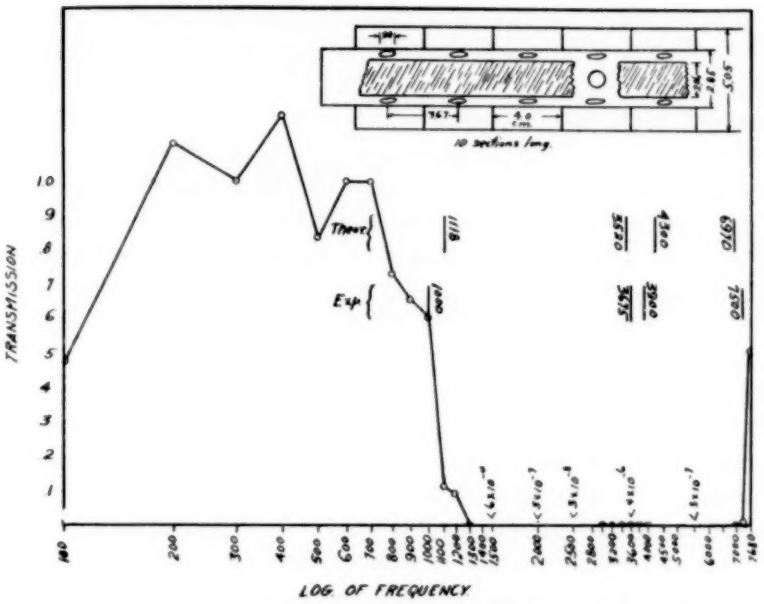

Fig. 2. An almost vanishing additional band in a low-pass filter.

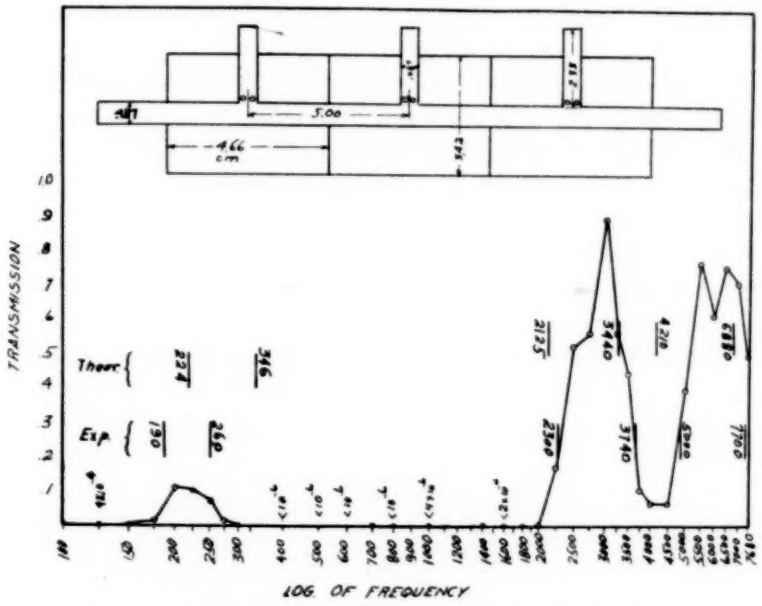

Fig. 3. A "single band" filter with two additional bands.

cases are selected not because of the excellence or inferiority of the filters as such but because they illustrate the agreement with theory. The experimental and theoretical values of the cut-offs are indicated on the figures and the agreement is found to be very satisfactory, the nature of the problem being considered.

Referring to the theorem that both Z_1 and Z_2 should have positive slopes when plotted with frequencies as abscissas, one can reach a conclusion concerning the location of the additional transmission bands relative to the resonance frequencies. Such a plot for low frequency-pass filters shows that in this region Z_2 is positive. Hence since the band extends between the frequencies where $Z_1/Z_2=0$ and $Z_1=-4Z_2$, and since Z_1 passes through zero from negative to positive with increasing frequency, the transmission band must be on the lower frequency side of the resonance value. In computations, this is not always true, presumably because of the approximate and semi-empirical character of the equations. For fifty-three bands computed for low-pass filters, only five did not have the resonance frequency as the upper limit and in each of these cases the band was very narrow. A similar graphical study of the single-band-pass filter shows that the resonance frequency is the upper limit of the additional transmission bands. No exception to this rule occurrs in the computed values of the transmission limits.

Conclusions

There has been given an approximate theory for the appearance of additional bands in low-pass and "single-band-pass" filters, the latter type of filter taking its name from the former theory.[1] This additional theory assists in design and at the same time affords an understanding of the phenomena.

I wish to acknowledge the assistance of Mr. R. V. Guthrie in the extensive observations and computations required for this paper.

University of Iowa.
May 23, 1924

VIBRATION OF A STRING UNDER INTERMITTENT IMPULSES

By D. Gunnaiya and G. Subrahmaniam

Abstract

Effect of a long obstacle slightly touching a vibrating string is to give it intermittent impulses with a frequency equal to that of the string. The equation of motion is given, and such impulses are shown to develop odd and even harmonics equally. The *tanpura* is such a case and was found by experiment to give equally prominent odd and even harmonics up to the fifteenth.

IN a recent article[1] K. C. Kar gave a theory of vibrating strings under intermittent impulses, the period of the impulse in his case being that of the octave. He observes that "if a hard substance is brought near the string at one of its ends from above or below so as slightly to touch it in its zero position and the string is then plucked at any point, it gives a note exactly similar to that of the tanpura." He concludes that the case of the tanpura is one of a string under intermittent impulses with the periodicity of the octave.

As to the period of the impulse, if the obstacle is the tip of the finger nail brought to touch the string in its equilibrium position, the string can travel past the obstacle and gets two oppositely directed impulses in the course of each period. Therefore, if no heed is paid to the sign, the period of the impulse may be said to be that of the octave; yet the effect is really that of unidirectional impulses with the frequency of the string. If the obstacle be rigid and extend on either side transversely to the string, for instance a pencil held with its length perpendicular to that of the string, the period is clearly that of the fundamental. It is the latter case that obtains in the Indian tanpura.

If a string is acted upon by an intermittent impulse acting at $t=0$, τ, . . . $n\tau$, the value of any one of the normal coordinates, ϕ_s, at time $(n+e)\,\tau$, where $e<1$, is given, as stated by Kar, by

$$\phi_s=\frac{2u_s}{lp_s}e^{-b_sT}\left[e^{-b_sn\tau}\sin p_s(n+e)\tau+e^{-b_s(n-1)\tau}\sin p_s(n-1+e)\tau+\right.$$
$$\left.\cdot\cdot\cdot\cdot+\sin p_sT\right],$$

[1] K. C. Kar. Phys. Rev. **21**, 672 (1923)

where $e\tau = T$ and u_s is the velocity imparted to the string by each impulse. When the period of the impulse is that of the string, $p_s\tau = 2\pi s$. Thus when n is large

$$\phi_s = \frac{2u_s}{lp_s} e^{-b_s T} \sin p_s T \left[1 + e^{-b_s \tau} + e^{-b_s 2\tau} + \cdots \right] = \frac{2u_s e^{-b_s T}}{lp_s (1 - e^{-b_s \tau})} \sin p_s T ,$$

whether s is odd or even. If the impulse acts at $x = x_0$, $u_s = u \sin (s\pi x_0/l)$. The equation of the string thus becomes

$$y = \sum_1^\infty \sin \frac{s\pi x}{l} \cdot \frac{2}{lp_s} \cdot \sin \frac{s\pi x_0}{l} \cdot u \frac{e^{-b_s T} \sin p_s T}{1 - e^{-b_s \tau}} .$$

From the above equation it follows that the amplitudes of all harmonics depend on the factor $1/(1-e^{-b_s T})$ and that when the b_s's are small it becomes ∞ for all harmonics and not for even harmonics only as in the case worked out by K. C. Kar.

The presence of all the harmonics was established experimentally by first plucking the string of the tanpura and then damping it at the proper node, when they could be clearly and persistently heard. The odd harmonics are as prominent as the even ones, and as a matter of fact, it is some of these odd harmonics that linger to the last. All the harmonics up to the fifteenth are recognized unmistakably by the above method.

The relatively small intensity of the fundamental is also suggested by the factor $1/(1-e^{-b_s T})$ which occurs in our equation. The b_s's are no doubt small and get smaller progressively for higher harmonics, the largest value being that for the fundamental. Thus the factor which tends more and more towards infinity for higher harmonics, has a finite minimum value for the fundamental.

RESEARCH LABORATORIES,
H. H. THE MAHARAJAH'S COLLEGE,
VIZIANAGARAM.
March 10, 1924.

COMMUNICATIONS

A Question as to the Value of Some Evidence Adduced by Nolan to Prove the Existence of Groups of Normal Ions in Air at Atmospheric Pressure

IN a recent article in the Physical Review Prof. J. J. Nolan[1] claims to have proven the existence of groups of ions having different mobilities. This proof is based on the assumed reality of certain irregularities or bends observed by Nolan in his current-voltage mobility curves. In an earlier article on mobilities using essentially the same method as that of Nolan, the writer[2] stated that in his long experience with this method he had on carefully controlled mobility curves never observed irregularities of the Nolan type. In his recent article Nolan reproduces one of the writer's curves plotted to a different scale and finds bends which he says correspond to some of his classes of ions. The writer does not feel that he can let this treatment of the data pass without a comment. The writer's data used by Nolan were taken with some care. In such electrometric measurements it is however almost impossible to avoid irregular readings of various sorts (e.g. such as are caused by small deflections produced by static charges from the platinum contact switches). Such irregularities were always present and the writer has data to show that repeated readings taken at one potential have variations which are ample to account for all the bends discovered by Nolan in this curve. Thus Nolan's use of the writer's bends is open to serious question.

The writer would also like to state that before evidence based on irregularities in curves can seriously be accepted as evidence proving any theory, it is essential that the variability of the readings due to instrumental irregularities be shown to be markedly less than the variations supposed significant. In Nolan's case it is necessary for him to show that a repeated reading at a given potential over the time of an experiment varies less than the departure of his points from a smooth curve. Until he does this his conclusions cannot be accepted.

Leonard B. Loeb.

Physics Department,
University of California,
Berkeley, California,
October 24, 1924.

[1] J. J. Nolan, Phys. Rev. **24**, p. 22 (1924)
[2] L. B. Loeb, Jour. Franklin Inst. **196**, 546 (1923)

Note on an Extension of Bohrs Correspondence Principle to Apply to Small Quantum Numbers

As pointed out by F. C. Hoyt, E. C. Kemble and R. C. Tolman the theorem proved by the writer in a recent article[1] for the case of circular orbits, is a special case of a more general principle given by Kramers. The importance of the theorem, however, makes the additional presentation not entirely amiss, especially in view of the emphasis which was placed on the mechanical interpretation of the principle. The work by Hoyt and others on intensities should provide a means of determining whether the equation of the spiral between stationary orbits is $ds = kdn$, as suggested in the abstract of the paper, or some other equally possible relation.

P. W. Ketchum

University of Illinois,
November 26, 1924.

[1] P. W. Ketchum, Phys. Rev. **24,** 463 (November 1924)

BOOK REVIEWS

A Treatise on Light. By R. A. HOUSTON. First edition 1915, new editions 1921 and 1923.—In the preface of the last edition the author says, "The present edition differs from the first one in having two colored plates, a new index and a short chapter on recent advances; also, owing to the courtesy of various correspondents, I have been able to make slight improvements throughout the work." One of the colored plates referred to, a frontispiece showing various types of spectra, was included in the *new impression* of 1919. The curious yellowish appearance between the green and the blue of some of these spectra is very noticeable. The new colored plate taken from Ganot's Physics and appearing in this edition for the first time shows six views of colored rings produced by polarized light in doubly refracting crystals. Space for insertion of a short paragraph explaining what each view represents was obtained by the omission of one of the four examples heretofore appearing on the page opposite. Except for a short supplementary index of topics discussed in the new chapter on recent advances, the more complete index [about twice as many items] was incorporated in the 1921 edition. A new chapter of seven pages on Recent Advances discusses Determination of Angular Diameter of Stars, the Half-Watt Lamp, the Neon Lamp, Einstein Star Shift, the Quantum, and Moseley's Work on X-Ray Spectra. It is regrettable that other topics dealing with modern developments in light have not been included; especially is this true of the recent advances in spectroscopy.

The merits of the book, of which there are many, are well known to students in this field. It has served to give an excellent preparation for further and more detailed study of the various subdivisions of the subject. Inaccuracies of statement have been unusually few. As indicated by the quotation from the author's preface clearness has been added by slight changes in wording here and there throughout the text.—Pp. XI+486. Price $4.00. Longmans, Green and Co., 1924. R. C. GIBBS.

A System of Physical Chemistry. Volume III; Quantum Theory. By WILLIAM C. McC. LEWIS. Third edition with certain appendices by James Rice, A. M'Keown, and R. O. Griffith.—This familiar book on the quantum theory has been enlarged and amplified to almost exactly twice the size of previous editions. As before, the book opens with a good non-technical account of some principles in statistical mechanics. Chapter II is devoted to the Planck radiation law, and Chapters III and IV to specific heats and infra-red absorption spectra. In presenting experimental material on the specific heat of hydrogen at low temperatures, Prof. Lewis says "It is impossible at the present time to account quantitatively for Eucken's results." This statement seems scarcely to do justice to the quantum theory of the molecular heat of gases developed by Reiche, Kemble, and others, which is mentioned only in a casual reference in a later chapter. A very interesting section, however, is included on the "degradation of gases."

Chapter V is devoted mostly to the Bohr theory of atomic structure, but also contains an account of Parson's magneton, the Langmuir inverse cube force, and Whittaker's magnetic wheel. Throughout much of the book one finds presented various versions of the quantum theory, differing widely in merit. It is thus perhaps doubtful whether all readers will recognize and esteem especially the particular developments which are legitimate applications or logical outgrowths of the Bohr-Sommerfeld quantum conditions.

Chapters VI to IX inclusive contain in particular much material not found in the earlier editions. Chapter VI deals with vaporization, thermionics, and photo-electricity.

Here the pages on contact electromotive force are very welcome. Chapter VII is especially valuable, for it devotes considerable space to quantum theories of chemical reactions. The two last Chapters VIII and IX are on Born's crystal lattices and on chemical constants, the Nernst heat theorem, etc. The "symmetry number" introduced by Ehrenfest, Trkal, and Fowler is unfortunately omitted as a factor in the formula (2) on p. 289 for the chemical constant of a diatomic molecule. The book closes with eight appendices, including one on the correspondence principle.

Prof. Lewis' book is lucidly written but can scarcely be regarded as an entirely accurate or up-to-the-minute account of the portions of the quantum theory which relate to theoretical physics. The greatest strength of the book lies rather along the line of physical chemistry. Here the volume contains much valuable subject matter, especially experimental, which is not contained in the usual treatises on the quantum theory of atomic structure.—Pp. x+407, price $5.00. Longmans, Green, and Co., 1924.

J. H. VAN VLECK

Colloid Chemistry. By JEROME ALEXANDER, Second edition, revised and enlarged. —This little book is intended to be used as an adjunct in teaching colloid chemistry. After six chapters on general theory, the author has eight chapters on the practical applications of colloid chemistry. In these eight chapters the subheads are: Astronomy; meteorology; smokes, fogs, and dusts; perfumes; geology; mineralogy; gems; agriculture; clays; ceramics and refractories; flotation; dyeing; shower-proofing fabrics; nitrocellulose and its products; celluloid; explosives; paints, pigments, and varnishes; emulsions; soaps; lubrication; coal; colloidal fuel; petroleum; asphalt; firefoam; insecticides; filtration; sewage disposal; photography; brewing; tanning; paper; rubber; foods and their preparation; baking; milk; ice cream; confectionery; gelatine and glue; glasses; metals and alloys; electrodeposition of metals; boiler scale; cement, mortar, and plaster; chemical analysis; pharmacy and therapeutics; antiseptics and bacteriology; biology and medicine; enzymes; cytology; growth; evolution; physiology and pathology; capillary circulation; psychiatry; anaphylaxis and immunity; healing of wounds; digestion; absorption; secretion, excretion; diagnosis; chemo-therapy and colloid therapy; serum therapy; plants; bio-electric currents.

From this summary it is clear that anybody who reads this book will get information on a large number of topics. The reviewer commends to the physicists the problem on p. 115 that photographic emulsions transmit reddish light when the silver bromide grains are less than one-tenth micron in diameter and green (or blue) light when the particles are over five-tenths micron. This same problem occurs with Porter and Keen's coagulating sulphur and with Piazzi Smyth's blue sun. In spite of a brave attempt by Raman, there is no satisfactory theory as to the transmission of green or blue by a system containing coarse but colorless particles. Pp. 216; price $2.00. Van Nostrand, New York, 1924.

WILDER D. BANCROFT

Storage Batteries. By GEORGE WOOD VINAL.—The book is a general treatise on the physics and chemistry of secondary batteries and their engineering applications. After a description of materials and methods of construction, the author gives a full and very adequate discussion of the electrolyte, transformation of energy and theory of reactions. Particular attention is given to the "double sulphate" theory, other theories being briefly mentioned. The latter half of the book deals with practical aspects of operation, efficiency and methods of testing. As the author states, he has drawn liberally on test reports and papers published by himself and his collaborators at the Bureau of Standards.

The wealth of material is well selected and well presented; the treatment thorough. Pp. VIII+402, 156 illustrations. Price $4.50. Wiley and Sons, 1924.

FREDERICK BEDELL

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE ANN ARBOR MEETING, NOVEMBER 28 AND 29, 1924

The 129th regular meeting of the American Physical Society was held in Ann Arbor, at the University of Michigan, on Friday and Saturday, November 28 and 29, 1924. The presiding officer was Professor Charles E. Mendenhall, President of the Society.

On Friday evening the members of the Society were the guests of the University at a dinner at which the speakers were Dean J. R. Effinger and Professor Mendenhall. The special feature of the meeting was the inspection of the new Physics Laboratory of the University of Michigan which was on exhibition during the meeting.

The meeting of the Council was held on Friday, November 28. The following elections were made: *transferred from Membership to Fellowship*, William Stubbs James and J. H. Van Vleck; *elected to Membership*, G. B. Abbey, Muriel F. Ashley, Collis M. Bardin, Philip Mark Barr, M. Watson Bingham, Leland Jaynes Boardman, Edward N. Bowie, Richard M. Bozorth, Charles J. Brasefield, F. G. Brickweddi, Harold Arthur Brown, Hugh Monroe Brown, Francis N. Cady, Emmett K. Carver, Nelson Perry Case, M. G. Christie, John L. Clark, Edward Condon, J. Horace Coulliette, C. G. Cullen, Philip Dalton, Leo I. Dana, Ona K. DeFoe, W. H. Dehlinger, Ralph G. Demaree, Hiram W. Edwards, Herbert A. Erf, Paul B. Findley, Nathaniel H. Frank, E. M. C. Guyer, Hallett N. Germond, G. Norris Glasoe, George Glocker, Theodore B. Godfrey, Jerome B. Green, Harry E. Hammond, J. D. Hanawalt, William J. Harker, Vincent E. Heaton, Donald E. Higgins, Kazuo Bert Hirashima, A. W. Horton, Jr., Theodore A. Hunter, Wilfrid James Jackson, A. Frances Johnson, Edwin John Knapp, John B. Lalime, H. L. Lillie, Charles Lithgow, William Harold McCurdy, Archie J. McMaster, William W. Macalpine, J. J. Mahoney, Italus Mei, Frank Charles Mock, Waldemar Noll, Fay Edison Null, Gwilym E. Owen, George Porter Paine, H. B. Peacock, T. Peczalski, Robert L. Petry, Franklin E. Poindexter, David Chandler Prince, Earle Keith Pyler, Robert R. Riesz, Conrad K. Rizer, Howard W. Russel, Henry Ruzicki, Felix Saunders, Myron M. Schwarzschild, David Sinclair, Clarence R. Smith, Andrew

J. Sorensen, Nelson E. Sowers, Erwin W. Tschudi, Merriam Hartwick Trytten, Francis Brooke Vodges, Fred Weinburg, Deane R. White, William Braid White, J. Warren Wright.

The regular scientific section consisted of 46 papers. Abstracts of these papers are given in the following pages. Papers Nos. 9, 17, 21, 23, 27, 34 and 35 were read by title.

HAROLD W. WEBB,
Secretary.

ABSTRACTS OF PAPERS

1. A short wave-length x-ray spectrograph and some K series emission wave-lengths. J. M. CORK, University of Michigan.—Accurate measurements of the K series emission wave-lengths of elements having atomic numbers greater than 52, have been reported only for tungsten (74) and platinum (78). Using an x-ray tube and an x-ray spectrograph, both of special construction, certain elements in this field have been investigated. The x-ray tube was of the hot cathode type, water cooled, with both cathode and anode removable at ground glass joints. The spectrograph was similar to that used by Rutherford and Andrade for γ rays, with a narrow slit interposed between the calcite crystal and the photographic plate. The advantages of the spectrograph and the accuracy attained are discussed. K emission wave-lengths are given for the following elements: Ba(56), La(57), Ce(58), Pr(59), Nd(60), Sm(62), Gd(64), Dy(66) and Er(68).

2. Determination of certain outer x-ray energy levels.. KATHERINE CHAMBERLAIN and GEORGE A. LINDSAY, University of Michigan.—The three L absorption edges for ten elements from antimony to samarium inclusive were photographed with a Siegbahn spectrograph together with the corresponding adjacent emission lines on the same plate. The values of $(\nu/R)^{\frac{1}{2}}$ for outer levels, obtained from differences between edges and lines, when plotted against atomic numbers, give curves which show a distinct change of slope at the beginning of the rare earth group. This confirms the Bohr theory that here electrons begin to be inserted into inner groups which were previously only partially filled. The curve representing the $O_{2,3}$ level is nearly horizontal for elements above La(57). Nearly all of the plates of L_3 and many of those of L_2 show a distinct white line on the short wave-length side of the absorption edge, which indicates there a region of especially great absorption. The absorption edges are much less distinct for those elements just below Xe(54) than for those above.

3. The M series of tungsten. R. V. ZUMSTEIN, University of Iowa.—Using a metal x-ray tube and a vacuum spectrometer, the emission spectrum has been investigated from 7 A to 5 A. Faint emission lines were observed at 6.948 A, 6.857 A, 6.789 A and 6.720 A. The first and fourth of these lines have been found by Hjalmar. No measurements were made on the strong α, β and γ lines. In the absorption spectrum, five lines were observed at 6.708 A, 6.475 A, 5.418 A, 4.800 A and 4.365 A. The first two are displaced from their predicted positions by an amount which appears greater than the limits of error. The third line has a component at 5.380 A. The fifth absorption line is very weak.

4. A search for element number 61. C. J. LAPP, R. A. ROGERS, University of Iowa and B. S. HOPKINS, University of Illinois.—A systematic search for element number 61 had been made by examining the L series x-ray lines from samples of rare earths carefully prepared by B. S. Hopkins. The Bureau of Standards had previously examined these samples and reported a large number of new lines in the arc spectra. A single very faint line which might be $L\alpha$ 61 was photographed; wave-length 2.285

A±.008. According to Cermak the Lα line of 61 should be 2.280 A. Everything possible was done to bring out this line more strongly but only a trace could be obtained although it appears on several plates. Judging from the intensity of the lines of manganese obtained when three parts in 1000 were present on the target, it is estimated that if element 61 was present it was in quantities of about 1 part in 2000 or less.

5. The x-ray analysis of certain alloys. WM. C. PHEBUS and F. C. BLAKE, Ohio State University.—With from 0 to 20 percent zinc, aluminum and zinc form solid solutions, the aluminum lattice decreasing from 4.0435 A to 4.0345 A. For between 20 and 95 percent Zn, the diffraction patterns of both components were obtained superimposed. The Zn lattice was not measurably distorted. No compounds were observed. Lead and tin formed solid solutions at room temperature, with from 0-3.6 percent Sn, the Pb lattice decreasing from 4.942 A to 4.931 A. For between 10 and 95 percent Sn the lattices of both components were present. The Sn lattice was not appreciably distorted. No compounds were observed. Chromium and nickel formed solid solutions with up to 60 percent Cr in the nickel lattice, the Ni lattice increasing from 3.521 A to 3.576 A. The distortion of the Al and Ni lattices were found to be proportional to the atomic percentages of the added solute. The solute atoms went into solution by displacing solvent atoms. The following forms and values of constants were found: Al, face-centered cubic. $a = 4.0435$ A; Zn, hexagonal close packed, $a = 2.664$ A, $c = 1.850$ A; Pb, face-centered cubic, $a = 4.942$ A; white tin, diamond tetragonal, $a = 8.235$ A, $c = 3.165$ Å; Cr, body-centered cubic, $a = 2.875$ A; Ni, face-centered cubic, $a = 3.521$ A. A method of correction for penetration was presented which holds over a range as great as from Al to Pb.

6. Measurements of the beta-rays excited by hard x-rays. ARTHUR H. COMPTON and ALFRED W. SIMON, University of Chicago.—Stereoscopic photographs of the β-ray trails excited in moist air by strongly filtered x-rays have been taken by the Wilson cloud expansion method. In accord with earlier observations by Wilson and Bothe, two distinct types of tracks are found, which we call *P* and *R* tracks. Using x-rays varying in effective wave-length from about 0.9 A to 0.1 A, the ratio of the observed number of *R* to that of *P* tracks varies from 0.10 to 72, while the ratio of the x-ray energy dissipated by scattering to that absorbed (photo-electrically) varies from 0.15 to 60. This close correspondence leads to the conclusion that just as each absorbed quantum of incident X-ray energy results in a photo-electron or *P* track, so each scattered quantum results in an *R* track. Measurements were made of the maximum range, the relative number of different ranges, the relative number ejected at different angles, and the relative ranges of the *R* tracks ejected at different angles by x-rays of different effective wave-lengths. The results agree closely in every detail with the predictions made by Compton and Hubbard assuming each *R* electron to recoil from an individual scattered x-ray quantum.

7. The alpha-ray track projector. H. T. PYE, McGill University (Introduced by A. S. Eve).—The well-known C. T. R. Wilson apparatus is admirable for photographic work and the Shimizu modification excellent for visual and other purposes. Hitherto it has been found impracticable to project α-ray tracks onto a screen by reflectoscope methods in order that a large audience may see them. In the present apparatus it has been found practicable to project the shadows of these tracks by ordinary methods. The expansion chamber of the usual piston-cylinder type has two plate-glass faces coated with glycerine and $CuSO_4$, between which a potential of 200 volts can be applied. Otherwise the general arrangement resembles that of the Shimizu apparatus. Light from a strong arc is reflected from a mirror, so that the expansion chamber may have its axis vertical, and a second mirror throws the light onto the screen, suitable

condensing lenses being employed. Other effects can also be projected, such as the spark discharge from points at various voltages in the expansion chamber.

8. The formation of alpha-ray tracks by simple means. CHAS. T. KNIPP and N. E. SOWERS, University of Illinois.—Alpha-ray tracks for lecture table demonstration purposes may be formed by means of exceedingly simple apparatus. A glass containing vessel blown into form from a pyrex beaker, a tiny source of alpha-rays mounted in a protected cavity at the inner end of an aluminum plug, a battery syringe bulb, a 100 to 200-volt B-battery, and a lantern for general illumination constitute the essential parts. The electrostatic field is set up between the surface of the water within the vessel and the freshly moistened inner wall immediately above it. The water should be made slightly acid to render it a better conductor. To operate the apparatus the electric circuit is closed permanently (no attention being paid to polarity or to earthing one pole of battery) and the hand bulb squeezed and released alternately until the proper ratio is obtained, whereupon the tracks will appear freely, being very distinct and persisting for some moments. The compression chamber being of relatively large diameter and of small height (the ratio being approximately 8 to 1) and free from projections within, insures minimum turbulency. The tracks may be projected upon a screen.

9. Half quanta and the stability of relativistic orbits. J. H. VAN VLECK, University of Minnesota.—It has often been contended that owing to relativity corrections an electron of azimuthal quantum number k would spiral into the nucleus if the atomic number Z exceeded k/α, where $\alpha = 2\pi e^2/hc = 1/137$. Such considerations, however, take no cognizance of the "mass packing" which can be neglected in most of the orbit but which must be considered whenever the electron is extremely close to the nucleus. H. A. Wilson has suggested (Prof. Roy. Soc. **102,** 9, 1922) that when the nucleus and electron are close enough to cause an appreciable overlapping of their force fields, then half their mutual potential energy is to be regarded as moving with the electron. When the radius r approaches zero, the rest mass would on this view no longer retain the conventional value m_0, but would approach asymptotically the value $m_0 - (Ze^2/2c^2r)$. It can then be shown that the orbit is periodic, regardless of the magnitudes of Z and k. Consequently Wilson's assumptions vitiate the familiar argument against half quanta that spiral orbits would result for $Z > 68$ if we had $k = 1/2$. This does not remove difficulties arising from the finite dimensions of the nucleus, neglected above.

10. Harmonic analysis of electron orbits and the probabilities of the transitions involved in the spectra of the alkali metals. FRANK C. HOYT, National Research Fellow, University of Chicago.—By means of the general method for central orbits an approximation has been obtained for the coefficients in the Fourier series representing the motion of an electron which for a portion of its path penetrates into the interior of the atom. For the purpose of obtaining the approximation the orbit is supposed to consist of outer segments in which the motion is Keplerian joined by inner segments which the electron traverses in a very short time so that for the purpose of such an analysis the exact character of the interior motion is immaterial. The formula obtained gives the coefficients as a function of the major axis and eccentricity of the outer loop and the angle between two successive outer loops. All of these quantities may be estimated from the empirical values of the spectral terms, and on the basis of the correspondence principle an estimate is made of the probabilities of the various transitions occurring in the emission and absorption spectra of the alkali metals. This leads to certain expectations in regard to the intensities of emission and absorption processes which can be compared with experimental data.

11. Molecular structure of methane. DAVID DENNISON, University of Michigan (Introduced by W. F. Colby).—A study is made of the interatomic vibrations of the

methane molecule assuming the hydrogen atoms to form a regular tetrahedron. Vibration frequencies and intensities are identified with the infra-red absorption measurements made by Dr. Cooley. The rotation problem is also analyzed and the fine structure of the infra-red bands interpreted. The normal methane molecule is shown to possess an electronic angular momentum of $\frac{1}{2}(h/2\pi)$.

12. On molecular rotation. O. KLEIN, University of Michigan (Introduced by H. M. Randall).—It is well known that the lines of many band-spectra in the visible and ultraviolet region show a fine structure of the same order of magnitude as the complex structure in the ordinary series spectra. It is natural to look for the explanation of this fine structure in a precession of the electronic angular momentum with respect to the molecule, a view which seems to be supported by the behavior of the components in magnetic fields. In this paper, which originated from a discussion with Dr. E. F. Barker, an attempt is made to calculate the energy of the stationary states of a simplified model of a rotating diatomic molecule, in which the electronic angular momentum is assumed to perform a uniform precession around the axis of the molecule in the case where the molecule does not rotate.

13. Quantum theory analysis of the band system of the first negative Deslandres' group. CHAS. M. BLACKBURN, University of Chicago (Introduced by Harvey B. Lemon).—The first negative Deslandres' bands have been investigated on the basis of the quantum theory of band spectra. The measurements were made principally from a first order plate taken on the 21-foot Rowland grating. As a whole, both in fine and gross structure, this system comprises an extremely complete confirmation of the theory of the emission of band spectra by a simple di-pole molecule. Twenty bands from λ2190-2786 were found to belong to this system, and in 18 of them the structure was determined in detail, the other two being too faint to exhibit their structure. All of the bands are found to have exceedingly simple and very similar structures. Of particular interest is the fact that there is no evidence of a Q-branch in the structure of any of them. The band ν_0's have been assigned to a system scheme on the basis of the theory as given by Kratzer, and comprise a beautiful confirmation of this theory. The moments of inertia before and after emission are computed to be respectively 8.07 and 6.78, both $\times 10^{-40}$ gm cm^2, giving a change of about 16 percent. A three dimensional model showing the transitions responsible for both the fine and gross structure was exhibited.

14. Relations between certain comet tail spectra and the first negative Deslandres' group. HARVEY B. LEMON, University of Chicago.—Certain comets having irregular tails, e.g. Daniels and Morehouse, show band spectra atrributed to compounds of carbon not elsewhere observed in celestial objects. Fowler reproduced these in the laboratory with carbon-compounds at extremely low pressure, and Merton developed them later between carbon electrodes in an atmosphere of helium. Apparently neither of them attained sufficient intensity to reveal the detailed structure of the bands under high dispersion. It has been found that, using a long tube (R. W. Wood type) and partial pressure of 2 cm of helium and about 10^{-4} mm of the residual gases from activated carbon previously outgassed, the comet tail spectra can be produced with great brilliance. Furthermore, it has been found that the conditions developing them also develop in great intensity the first negative Deslandres' group. A preliminary report of the analysis on the basis of the quantum theory of the band spectra has been made by Mr. C. M. Blackburn. (See preceding abstract.)

15. Secondary standards of wave-length in the spectrum of iron. GEORGE S. MONK, University of Chicago.—Using a Fabry-Perot interferometer with auxiliary grating dispersion, wave-lengths of cadmium lines from a Michelson H-tube, a new form of tube, and an arc in vacuum have been compared. The red line of cadmium has been measured

in comparison with lines of neon. Then, using neon as a standard, the wave-lengths of the suggested secondary standards in the spectrum of iron have been measured. The source of the latter was a 12-15 mm Pfund iron arc operated at 5 amperes on a 220-volt circuit. Exposures have been made in air and in vacuum and the results compared. Certain stable iron lines suggested by the International Committee on Standards of Wave-length as substitutes for unstable secondaries have been measured and some substitutions are recommended. Mercury lines 5461, 5769, and 5790 are suggested as auxiliary standards in interference measurements of the kind described.

16. The vacuum spark spectrum of carbon, λ2200-λ6600. R. A. SAWYER and E. J. MARTIN, University of Michigan.—The line spectrum of carbon does not appear to be well developed in most ordinary light sources. The lines are few in number, broad and fuzzy. The authors, feeling that the vacuum spark should be a more satisfactory source, have investigated the vacuum spark spectrum of carbon using cocoanut charcoal as electrodes. The resulting spectrum contains, with few exceptions, the lines obtained by Eder and Valenta in the carbon spark, about 25 in all. All the lines assigned by Fowler to C^+ appear strongly. The lines are mostly sharp and easily measurable, several being resolved as close doublets. In addition, a considerable number of new lines appear. About 30 of these are of an intensity comparable to that of the previously known lines. The new lines are largely close doublets although a few appear as single lines and there are one or triplets.

17. Note on the absorption of λ2540 by mercury vapor. JOHN T. TATE, University of Minnesota.—Franck and Grotrian have shown that mercury molecules are responsible for the absorption band at λ2540. The experiments of van der Lingen and Wood, showing that mercury vapor just leaving the liquid surface fluoresces strongly while older vapor gives no visible fluorescence, suggests that the proportion of molecules is much greater in the former case. On this view the fresh vapor should absorb λ2540 much more strongly than the older. Experiment shows no observable difference and the conclusion is that the entities which are responsible for the visible fluorescence in freshly distilling vapor are not the molecules which absorb λ2540. Two experiments show conclusively that these latter are not heteropolar molecules formed between excited and neutral atoms. First, the intensity of the source has no effect upon the absorption, showing that the absorption is not a function of the number of excited atoms present in vapor. Second, the absorption persists when monochromatic light containing no frequency capable of exciting the normal mercury atom is incident on the vapor.

18. The low voltage arc in oxygen. L. L. LOCKROW, Linde Air Products Company and O. S. DUFFENDACK, University of Michigan.—A study of the oxygen spectra and of certain excitation potentials has been made by the low voltage arc method with the following results and conclusions: (1) Ionization of the molecule occurs at 16.1 volts. (2) The resonance potential at about 9 volts formerly assigned to the atom is a resonance potential for the molecule. (3) Dissociation of the molecule and simultaneous ionization of one atom occurs at 19.5 volts. (4) Doubly charged atomic ions first appear in the discharge at about 50 volts. (5) An initial state energy level of 19.2 volts has been found for the first negative bands which extend from 4870 A to about 2400 A. The final state level for these bands is at 16.1 volts. (6) The second negative band system appearing between 6583 and 4955 has the initial electronic energy level of 21 volts and the final state level is the same as the initial level for the first negative bands. A detailed analysis of the band systems of oxygen is being undertaken.

19. Low voltage arcs in phosphorus vapor. O. S. DUFFENDACK and H. HUTHSTEINER, Research Laboratory, General Electric Company.—Low voltage arcs were struck in phosphorus vapor obtained by heating red phosphorus in the discharge tube. The minimum arcing potential was found to be 10.3 volts which is also the voltage at

which ionization begins in a vapor containing a high percentage of atomic phosphorus. It is concluded that this is the ionizing potential of the phosphorus atom. The spectrum of the low voltage arc contains both lines and bands. The lines are those of the arc spectrum reported by Miss Saltmarsh (Phil. Mag. May, 1924). Her contention that the arc spectrum begins at λ2555 is supported. A new band spectrum was found in the region λ2200−λ2600.

20. Non-oscillatory abnormal low voltage arcs with reversed electric fields caused by ion diffusion. CARL ECKART, Edison Lamp Works, and K. T. COMPTON, Princeton University.—Following a suggestion by Langmuir that a reversed anode drop might account for the maintenance of non-oscillatory arcs at voltages less than the lowest critical potential of the gas, experiments were instituted in argon and mercury vapor which gave the following results. With the arc of about an ampere maintained on about 5 volts in argon, the cathode drop was always as large as the minimum radiating potential (11.5 volts), so that a reverse field of about 5 volts existed in the remaining part of the arc. The current passed in spite of this reverse field on account of the high concentration gradient. There were about 10^{10} electrons (and the same number of positive ions) per cc near the cathode and about 10^{13} per cc near the anode. The reversed field is due to this concentration gradient, combined with the fact that the mobility of electrons exceeds that of positive ions. Supplementary experiments disproved a suggestion that mercury vapor plays any essential part in abnormal low voltage arcs.

21. Doubly ionized atoms in mercury vapor. C. D. CHILD, Colgate University.—It has been found that mercury vapor that has been distilled past a hot cathode from which cathode rays are streaming is luminous, but that when such rays are not apparent, the vapor above the cathode is not luminous and vapor distilled past the positive column of the discharge is also not luminous. The glow here described is not a continuation of the cathode rays, but is no doubt due to the recombination of ions produced near the cathode, and carried by the vapor to other parts of the tube. Since the ions formed in positive column can not be carried to a distance before recombining, they can not be the same as those formed at the cathode. There are reasons for believing that in the positive column only singly ionized atoms are produced while near the cathode doubly ionized ones are produced, and that the doubly ionized atoms recombine with electrons much more slowly than do the singly ionized ones.

22. On the independence of the mobility and mass of an ion. HENRY A. ERIKSON, University of Minnesota.—The experimental fact that the mobility of an ion and its mass are quite independent is at this time unexplained. This fact comes into evidence when an ion is produced and passed into air for the determination of its mobility. In order to account for the above it seems necessary to assume that all natural complex molecules which have lost or gained an electron move with the same velocity when the gaseous medium and the applied fields are the same. This must mean that the mobility is determined by the charge, that the volumes of all complex molecules are not sufficiently different to give rise to any observable effect, and that the effectiveness of the field and the polarizing actions exerted by the charge upon the adjacent molecules are the same. As soon, however, as the one molecule ion draws to itself another neutral molecule forming an artificial structure the mobility becomes less. In this case the results, on the author's interpretation, show that an air ion two molecules large and a CO_2 ion two molecules large have the same mobility in air. The resistance to motion is the same for these two ions.

23. Apparent transmission of low velocity electrons through aluminum foil. HENRY E. HARTIG, University of Minnesota.—Aluminum foil .0003 cm thick was bombarded by electrons having velocities between 0 to 1600 volts. Using a single foil, electrons were observed to emerge from the reverse side for all incident velocities from 0 to 1600 volts.

A prominent maximum was obtained in the current curve at 8.5 volts, and a great number of smaller maxima were noted in the range from 20 to 100 volts. It is thought the latter maxima are associated with the structure of the soft x-ray spectrum of aluminum. The large maximum at 8.5 volts is of a different character, and suggests the possibility of a transparent atom effect in aluminum. The velocities of the emergent electrons for all incident velocities, were less than 10 volts. The transmission through two foils was only 1/10,000th part of that observed for one foil, and a third foil cut down the transmission by an additional factor of 1/10. The emergent electrons in the case of two and three foils are almost entirely photo-electrons liberated by soft x-rays generated by the incident electrons. In the case of transmission through only one foil, most of the emergent electrons have a different origin, and behave as though they are incident electrons which by collision have had their velocity reduced to a favorable value for traversing the foil and escaping.

24. The heat of evaporation of electrons. J. J. WEIGLE, Westinghouse Research Laboratory, University of Pittsburgh.—The assumption of spaces lattices of electrons in crystalline metals gives a good explanation of the thermionic emission. On this assumption the potential energy of an electron inside the metal should be equal to the work function or heat of evaporation. This energy may be calculated simply from the space lattice constant provided we know the distribution of the electrons in the crystal. The work function may be calculated also from the grating energy of the space lattice which determines the relative parts due to the positive ions and electrons respectively. We have $L_0 = V_R - V_{RX} r_n/(r_n + r_p) + a$ where L_0 is the heat of evaporation of one electron, V_R the grating energy of the metal R, V_{RX} that of the salt RX and r_n and r_p the radii of the positive and negative ions forming RX; a is the energy necessary to transform one crystal structure into the other. The values calculated for the alkali metals are for Na, 1.83 (1.82); K, 1.53 (1.55); Rb, 1.54 (1.45?); Cs, 1.34 (1.36); in volts per electron. Observed values are in parenthesis. V_R and V_{RX} are not known with sufficient accuracy for a very exact calculation of L_0 but the above values seem to support the theory that metals are constituted of ions and that the electrons form a space lattice just as negative ions do in ordinary salts.

25. Determination of e from measurements of shot-effect in high frequency circuits. ALBERT W. HULL and N. H. WILLIAMS, General Electric Co.—Probability fluctuations in thermionic emission are to be expected, similar to the well known fluctuations of alpha particle emission. Schottky has shown that the magnitude of these fluctuations (called by him Schrot- or shot-effect) should depend upon, and be a measure of the charge e of the electron. This prediction was confirmed, as to order of magnitude, by measurements of Hartmann. We have repeated these measurements, using a much higher frequency and a reliable measure of r.m.s. voltage, and obtain values of e which are accurate to about 1 percent, in full agreement with Millikan's value. The precision of these measurements can be greatly increased. Preliminary measurements have been made of the influence of space charge and secondary electron emission upon shot-effect. Space charge destroys the independence of individual electrons, and hence decreases shot-effect. Secondary electron emission gives full shot-effect, showing that there is a time-lag between impact and secondary emission. These results indicate the usefulness of shot-measurement as a tool.

26. Cold electronic discharge from molybdenum. ROBERT J. PIERSOL, Westinghouse Research Laboratory, East Pittsburgh.—This is a continuation of the work reported on at the Toronto Meeting of the British Association. The electrodes are made from molybdenum plates, 0.030 cm thick, pressed into hemispherical shells, 1.0 cm radius, and welded to tungsten rods, 0.283 cm diameter, which are sealed into a hard glass tube. The discharge gap is 0.023 cm. A cocoanut charcoal bulb is attached which

in evacuation is kept at 386°C. The electrodes are heated to 1400°C by an induction furnace, the tube is baked at 500°C, the outgassing covering forty-eight hours. The connected discharge tube and charcoal bulb is sealed off. The bulb is placed in liquid air and the discharge tube is heated at 500°C for two hours. Then the tube is slowly sealed off from the bulb. This shows a gradient of 5400 kv/cm at 20°C as compared to 1200 kv/cm when a charcoal vacuum is not used. Also the minimum discharge potential becomes sharply defined, being reproducible after a period of nine months. Preliminary work shows that increase in temperature, below thermionic range, increases the cold electronic current and lowers the breakdown gradient.

27. **The photo-electric response of potassium at low temperatures.** J. W. HORNBECK, Carleton College.—Carefully purified potassium in a highly evacuated tube surrounded by a double walled container for liquid air, insulated by wool, was illuminated with monochromatic light of constant intensity. As independently observed by Ives, the current wave-length curve at −180°C is shifted to shorter wave-lengths with respect to the curve at 20°C, the shift decreasing from about 500 A at the long wave limit 6500 A, to 80 A in the blue. These shifts are reversible and reproducible. Monochromatic heating and cooling curves run approximately parallel to the temperature axis except between −80° and −100°, where they show a sudden change. This region is where a change of crystal structure is known to take place. The shifts observed seem then to be due in part to the change of crystal structure. This point needs further study. Slight sudden changes of temperature produced irregular effects which are not understood; they may possibly be associated with the condensation of new vapor or with cracks in the surface.

28. **The extinction coefficients of certain liquids and Drude's "friction" term.** M. H. TRYTTEN, University of Iowa (Introduced by L. P. Sieg).—In setting up the equation of motion of the electron in an absorbing medium Drude used a term to take account of "friction." By working out the extinction coefficient for wave-lengths in the visible spectrum a method was found of determining this quantity. The quantity r which he assumes to be a constant of proportionality between the resistance to the motion of the electron and the first power of the velocity was found to be no such constant but to vary with the frequency. Curves showing the variation of r with λ were obtained for five liquids. Curves for the extinction coefficients for the range of the visible spectrum were also obtained.

29. **A method for the direct measurement of the velocity of migration of ions in a solution.** JOHN J. GREBE, Case School of Applied Science.—The migration velocity of ions is measured by determining the time required for these ions to travel a known distance in pure water under a measured potential gradient. The apparatus consists of a vessel covered with a porous diaphram and containing an electrolyte and an electrode. On this diaphram rests the end of a glass tube which is connected to a supply of pure water. Within this tube, and a few centimeters from the end is placed a wire mesh electrode. The tube is flushed and filled with water and a potential of several hundred volts is applied between the wire mesh and the solution. The initial current is due to the conductivity of the water. The current then increases steadily, due to the motion of ions from the solution into the tube. From the rate of increase of the current the velocity of migration of the ions is determined. The effects of diffusion, encosmose, heating of the cell, and time-lag of an automatic current analyzing device have been studied and reduced to a minimum. The results obtained check the calculated velocities closely.

30. **Hall effect and specific resistance in thin evaporated films of Fe, Co, Ni, Pd and Pt.** H. B. PEACOCK, University of Iowa.—Investigation of the Hall effect and specific resistance in thin films of evaporated iron, cobalt, nickel, palladium and platinum gives

the following results: (1) The "asymptotic" specific resistances range from 4 to 30 times the accepted values for the corresponding bulk metals. (2) The Hall coefficients for the paramagnetic metals, palladium and platinum, are slightly smaller than bulk values. (3) The Hall coefficients for iron, cobalt and nickel are 1.8, 5, and 7 times, respectively, the accepted values for the bulk metals. (4) Heating films of cobalt and nickel during deposition decreases both the Hall coefficient and specific resistance, indicating crystalline growth. (5) Saturation of the Hall effect occurs for cobalt at about the same magnetic field as for bulk (13000 gauss) and for nickel at 2500 gauss as compared with 6000 gauss in bulk. With the highest field used (17000 gauss) no saturation occurs in films of iron. (6) Microscopic investigation shows some evidence of crystal structure in films of nickel and cobalt. Results (1) and (2) are readily explicable by granular structure. Results (4) and (2) indicate that granular structure or probably size of crystals affects the Hall coefficient in ferromagnetic metals but not in others. This points out a difference worthy of study and indicates that the Hall phenomenon may be caused essentially by inhomogeneity.

31. Magnetic properties of thin films of ferrogmagnetic metals produced by the evaporation method. A. J. SORENSEN, University of Iowa.—Thin films of *iron, nickel and cobalt* were deposited by the evaporation method on tin or aluminum foil, and the magnetic properties studied by an induction method for fields up to 139 gauss. The thickness of the films varied from 20 to 300 millimicrons. The results are as follows: (1) The maximum value of the intensity of magnetization is of the same order of magnitude as for bulk metal. In the case of cobalt, however, it is evident from the curve that with higher fields values higher than any heretofore attained might be secured. The magnetization is independent of the crystal size and the thickness of the film. (2) The remanence is high for iron and cobalt. For nickel a low value was obtained, perhaps due to oxidation. The remanence depends on the crystal size but not on the thickness. (3) The coercive force is high for all three metals and changes abruptly to lower values as the thickness is increased beyond a critical value, which for iron, cobalt and nickel is about 55, 70, and 200 millimicrons respectively. The high values of the coercive force may be due to the minute size of the crystals in the films.

32. Non-magnetic films of nickel. L. R. INGERSOLL, University of Wisconsin.—Most cathode films of nickel, sputtered in hydrogen, show little or no magneto-optic rotation. In these films, tractive effects, when suspended in a strong magnetic field, are also lacking. However, after heating for an hour or two at about 300°C in a vacuum or hydrogen, the film exhibits the magnetic and magneto-optic properties one associates with this metal. Microscopic and other examinations of the films under many different conditions lead to the conclusion that the film is an aggregate of very finely divided particles, generally sub-microscopic in size, which coalesce under heat treatment into larger units. This definitely indicates a dependence of magnetic properties on the size of particle. The crystal structure of the film is now being investigated. In some cases, particularly when the film is sputtered on a surface at liquid-air temperature, remarkable color effects are observed. These duplicate some of the phenomena found by Wood for granular films of sodium and potassium, but their explanation is not certain.

33. Effect of superposed alternating current on apparent magnetic permeability and hysteresis loss. T. SPOONER, Research Laboratory, Westinghouse Elec. and Mfg. Co., East Pittsburgh.—(1) *D.c. and a.c. fields parallel.* It is often assumed that when an a.c. magnetizing force is superposed on a d.c. magnetizing force, the permeability of the magnetic material is increased and the hysteresis loss decreased due to the shaking up action of the alternating current on the magnetic particles. An attempt is made to show theoretically and experimentally that these effects are only apparent, as the true permeability and hysteresis remain approximately the same as under d.c. conditions. What are

actually measured are the midpoints of displaced minor hysteresis loops. From the known laws of variation of these minor loops the apparent magnetization curves and hysteresis loops under superposed alternating current can be calculated. The method of doing this is illustrated. Under these assumptions superposed alternating current actually increases the hysteresis loss instead of suppressing it as has often been assumed, the resulting hysteresis consisting of that due to an increased major loop plus the losses due to displaced minor loops. (2) *D.c. and a.c. fields at right angles.* Some consideration is given to this case but at present it is not susceptible to quantitative calculations.

34. Anhysteretic magnetostriction effects. PAUL MCCORKLE, Western Reserve University.—A careful study was made of the effect of tension on the intensity of magnetization, and the effect of longitudinal magnetic field on the change of length, using specimens of *iron, nickel and cobalt.* Only small magnetic fields were used. The cobalt wire was an especially pure specimen (99.73%). Because of earlier complex results, especially in the case of iron, and in order to test the well known thermodynamical relation $(\partial I/\partial T)_H = (\partial l/\partial H)_T$, which is only valid in the absence of hysteresis, an alternating field was superposed to eliminate this complication. The study of the effect of tension on intensity of magnetization showed that the reversal effect in iron was a temporary one, the permanent effect being a continual decrease. Nickel and cobalt gave the customary decrease but with smaller fields. In the change of length effect, iron gave the usual increase to a maximum. This increase was greater at low fields but the total change was no greater. Nickel gave the customary decrease in length. This change was greater in low fields but as in iron the total change was the same. The effect in cobalt was too small for measurement in the largest fields used, 30 gauss.

35. Recent Determinations of the Magneton. J. KUNZ, University of Illinois.—Several new formulas have recently been proposed for the calculation of the magneton of Bohr by various applications of space quantization of the electronic orbits. The best experimental values of the magnetic moments are tested by these formulas and it is found that the difference between the various formulas and the experimental values lies between 4 and 6 percent, and is larger than is compatible with the accuracy of the measurements. The Bohr magneton seems not yet to be established by the determinations of paramagnetic susceptibilities.

36. Criticism of the Whittaker atomic model. JOHN A. ELDRIDGE, University of Iowa.—Whittaker has suggested as a model atom a "magnetic wheel," consisting of a number of radial magnets like poles grouped at the center. Such a mechanism was supposed to be able to absorb energy in quanta from an electron approaching the wheel along the axis of symmetry. The present paper points out that Whittaker arrived at this result only by neglecting the torque upon the central magnetic poles. To make the model work Whittaker must assume unipolar magnets, an assumption not in accord with physical experience.

37. The torques between cylindrical coils carrying rapidly varying alternating currents. THEODORE A. HUNTER, University of Iowa, (Introduced by G. W. Stewart). —The present investigation is a continuation of an investigation by W. A. Parlin (Phys. Rev. **22**, 193, 1923) who measured the torques and forces between coils carrying currents of radio frequency, i.e. frequencies from 10^4 to 10^7, and found that in certain cases the forces increased with the frequency of the current, when other factors such as current, distance apart of the coils, etc., were maintained constant. This result was not to be anticipated from the classical formulas of Maxwell and the cause and effect were not evident. In the present work measurements of the torques between coils of various dimensions have been made for currents of frequencies varying from 10^6 to 7×10^6. The results of Parlin were substantiated in every detail, but a different explanation of the

results is given. The measurements were carried out for wave-lengths approaching the natural wave-length of the coil combination. The data suggest that the increase in the torque with the shorter wave-lengths is to be attributed to the effect of the distributed capacity of the coil combination.

38. Power losses in solid dielectrics. C. F. HILL, Research Laboratory, Westinghouse Elec. and Mfg. Co., East Pittsburgh.—Data have been obtained at frequencies corresponding to from 400 meters to 3000 meters wave-length for N and K for lead glass at temperatures up to 220°C, N being Schweidler's constant in the equation for dielectric absorption, and K being the exponent in the equation $R = Af^{-K}$, where R is the effective series resistance of a condenser. The variations of N and K with temperature have been determined. The results are considered as pointing to an ionic displacement theory of dielectric absorption and dielectric power loss.

39. The optical constants of magnesium and of zinc crystals in the visible spectrum. M. E. GRABER, University of Iowa.—Results of an experimental study of the optical properties of magnesium and zinc in the form of single hexagonal crystals are presented. The method of procedure was that employed in the extended researches on crystal optics conducted at the University of Iowa. Plane polarized light at an azimuth of 45° was reflected from one of the six plane faces of the crystal which was placed in two principal positions. In the first position the principal axis of the crystal was perpendicular to the plane of incidence, and in the second position it was parallel to the plane of incidence. Two sets of optical constants (index of refraction, absorption index, and reflecting power) were obtained for each metal. Both indices of refraction for magnesium were found to be less than 0.5 for the range of wave-lengths studied. The indices for zinc were found to be greater than unity excepting for the shortest wave-lengths employed. The reflecting powers of both metals agree well with the comparison determinations available. No marked selectivity was found in the optical properties for either metal.

40. The crystalline nature of a sputtered tellurium film. L. P. SIEG, University of Pittsburgh and M. E. GRABER, University of Iowa.—Microscopic examination of a sputtered tellurium film failed to yield any information as to the crystalline character of the deposit. The deposit may consist (1) of granules of the metal, (2) of small crystals oriented at random, or (3) of crystals few or many in number with some definite orientations predominating. A test was made by reflecting plane polarized light at azimuth 45° and at 70° incidence, and subsequent analysis of the reflected elliptically polarized light. Two arbitrary settings of the film were made, in one of which the plate bearing the film was rotated 90° in its own plane. The resultant analysis showed that the reflected elliptically polarized light was quite different in the two cases, and pointed to the third possibility stated above as being probably the one representing the facts.

41. An application of the neutral wedge in a form of direct comparison spectrophotometer. H. C. TERRY, University of Chicago.—An arrangement using a Brace prism or a Lummer-Brodhun cube with a dispersing prism, is described, in which the intensity of the comparison source is varied by means of a pair of neutral wedges, thus eliminating the necessity of an intermediate comparison source. The method of application of this instrument to the detection and measurement of a shift in the phosphorescent or fluorescent spectra accompanying photochemical changes in certain luminescent substances is given. The paper includes a standardized method for making neutral gelatin wedges and also gives the results of an investigation of a number of the so-called neutral dyes.

42. Variation of Young's modulus with temperature from vibration measurements. A. L. KIMBALL, JR., and D. E. LOVELL, Research Laboratory, General Electric Co.—Measurements were made of the frequencies of tuning forks two feet long, made of

3½% nickel steel and of commercial carbon steel, at temperatures ranging from 20°C to 500°C. The fork under test was placed in an asbestos box heated by electric coils. At the desired temperature, which was recorded by thermometers, a clip was pulled off the end of the fork and its vibration was recorded by a stylus upon a moving smoked glass plate. The recording stylus was directly connected to the tuning fork by a fine wire. Time was simultaneously recorded by another stylus which marked seconds from a pendulum. The advantage of this method lies in its accuracy and freedom from the errors to which static deflecion methods are subject due to slight plastic yielding and elastic after effects. The effect of the small damping friction upon the frequency is a negligible quantity. The 3½% nickel steel, whether heat treated or annealed, and the carbon steel all showed practically the same decrease of elastic modulus with temperature, which followed a slightly falling curve. At 400°C Young's modulus was found to be about 12 percent less than at 20°C.

43. Absorption of high frequency sound. D. L. Rich, University of Michigan and W. H. Pielemeier, Pennsylvania State College.—One term in Lebedew's theoretical expression for the absorption constant of sound in air involves the dissipation of energy within the molecule. Neklapajeff's experimental value of the absorption constant for air is approximately twice Lebedew's theoretical value. A more precise measurement of this constant was attempted. Numerous sources of high frequency sound were tested with the object of obtaining a sound "beam" of constant and sufficient intensity to make reliable absorption measurements. Of the tested sources a piezo-electric tone generator giving waves of plane wave front proved best adapted to the purpose. It was constructed of quartz and aluminum. Sound waves proceeding from the tone generator operated a pressure vane whose deflections were observed. Our experimental determinations lie between Lebedew's theoretical value and Neklapajeff's experimental value. The deviations of both experimental values from the theoretical one are probably due to carbon dioxide in the air. It was found that additional amounts of carbon dioxide increased the absorption enormously for all frequencies tested. With approximately pure carbon dioxide no deflections could be obtained. The precision is not sufficient to yield useful data on the absorption within the molecule but it reveals the interesting fact that carbon dioxide has practically a total absorption band in the region near 100,000 vibrations per second.

44. Influence of a branch line upon acoustic transmission. G. W. Stewart, University of Iowa.—It is well known that any branch attached to a transmitting acoustic conduit will affect the energy transmitted, and it is the purpose here to establish the general formula for the energy transmitted in terms of the impedance of the branch. The ratio of the energy transmitted with the branch present to that with the branch absent is found to be $[(Z_1^2+Z_1\rho a/2s+Z_2^2)^2+(\rho a Z_2/2s)^2]\ [(Z_1+\rho a/2s)^2+Z_2^2]^{-1}$ Herein the point impedance of the branch is Z_1+iZ_2, ρ is the density of the fluid, a the velocity of sound and s the area of the conduit. This general formula is applied, by way of illustration, to two cases: The branch being a Helmholtz resonator and the branch being a closed cylindrical tube. The above ratio in these cases becomes, respectively, $\{1+[4s^2(h/c-1/hV^2)]^{-1}\}^{-1}$ and $(1+\sigma^2\tan^2 kl/4s^2)^{-1}$. Here c is the conductivity of the orifice, k is 2π divided by the wave-length, V the volume of the chamber, σ the area of the tube and l its length. The experimental and theoretical values of the transmission ratio over a large range of frequencies show an agreement within experimental error.

45. Investigation of acoustic double resonators. F. R. Watson, K. H. Hubbard, and F. E. Hubbard, University of Illinois.—Measurements were taken to determine the resonant frequencies of double resonators for various volumes of the single resonating chambers. A Rayleigh disk suspended in the neck connecting the two component

resonators allowed quantitative tests. A portable instrument was constructed by which a sound of a definite pitch could be measured conveniently in different locations in a room.

46. A method for the production and measurement of longitudinal sound vibrations in a rod. WILLIAM D. CROZIER, University of Iowa (Introduced by C. J. Lapp).—In connection with the investigation of acoustic wave filters in solid media, such as were reported upon by V. C. Hall, an electrical method has been developed for producing longitudinal sound vibrations in a rod and measuring their intensity. The vibrations are produced by applying the output of a vacuum tube oscillator with a power amplifier, to a device attached to the end of the rod, which is similar to the Fessenden oscillator used in submarine sound signalling. Intensity measurements are made by the voltage generated in a remodeled magneto-telephone receiver attached to the rod. This voltage is applied to a vacuum tube amplifier, the output of which is measured by a thermocouple and galvanometer. The present work did not require the measurement of absolute intensity, but the transmission of the filters was determined by comparing the intensity with the electrical input to the oscillator. This comparison was effected through the use of a calibrated mutual inductance.

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